The Physical and Chemical Evaluation of Airborne Coal Mine Dust

by

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A thesis submitted to the University of Glasgow in fulfilment of requirements for the award of the degree of Ph.D. in the Faculty of Science.

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INTRODUCTION

The work described in this thesis is part of a dust research programme carried out in the Department of Chemical Technology of the Royal College of Science and Technology and is a preliminary attempt to relate the incidence of lung disease in various Scottish coal mines with the environmental conditions existing in these mines. Work of a similar nature is being carried out by the National Coal Board at the Safety in Mines Research Establishment, Sheffield and in various National Coal Board laboratories throughout the United Kingdom. It was intended to collect a fairly large number of dust samples underground using a suction apparatus containing a Soxhlet thimble (1) and to subject these samples to various tests so that the silicosis hazard due to their presence could be evaluated. It was also intended to estimate the chemical composition of those samples by a method which would not lead to the inevitable counting error encountered by previous workers using purely optical techniques (2)

A suitable statistical treatment of the results should have indicated whether coal miners' pneumoconiosis was indeed a modified form of silicosis, or whether it was caused almost entirely by the amount of dust inhaled by the victim. Alternatively, if statistical analysis failed to show either the quantity of dust present or the silicosis hazard of the dust to be connected with the incidence of lung disease, added strength would be given to Evans' theory (3) that the lung disease contracted by coal miners is due more to the type of coal dust present than to any other single factor.

It was found necessary to devote considerable time to developing methods of sample examination which gave sufficient accuracy, and were both reasonably rapid and economic in dust. As a result,

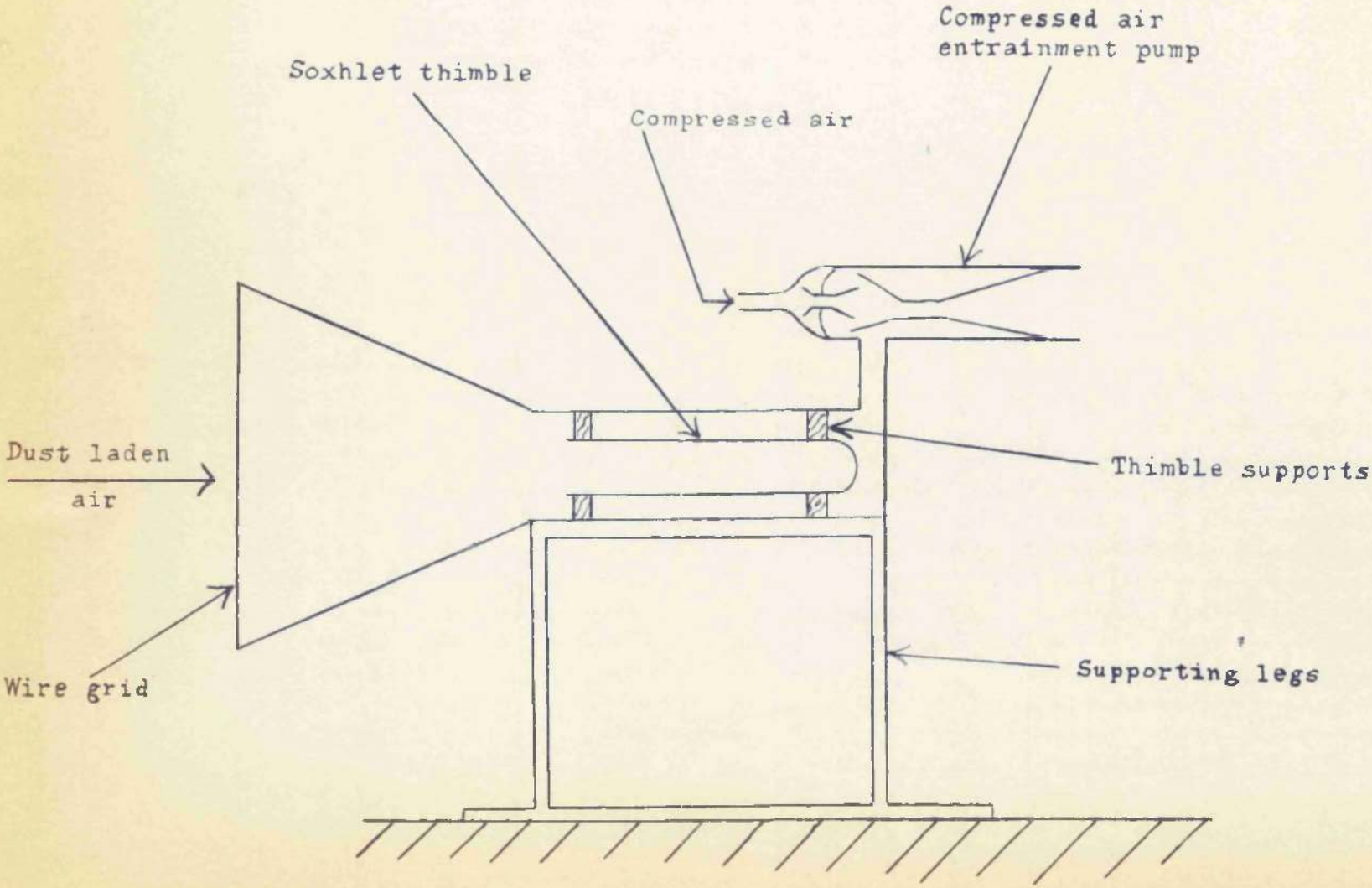
insufficient samples were in fact analysed to permit a worthwhile statistical survey, although a fairly clear idea of the typical type of airborne dust present in coal mines was obtained and progress was made in deciding which tests could most suitably be applied in evaluating the silicosis hazard due to the dust.

The silicosis hazard of the dust depends upon two independent factors: physical factors mainly related to particle size, and chemical factors mainly related to free silica content. The techniques adopted in estimating the various properties of the airborne dust are therefore described in two separate sections, each dealing with one of these factors.

Fig 1

Schematic Drawing of H - J Macro Dust Sampler

(Section through centre)



METHOD OF DUST COLLECTION

Design of Dust Collector

The dust samplers employed were built to a design by Hunter and Jaap (1) and, all but the prototype which was constructed in this Department, were fabricated by the National Coal Board workshops. Each collector consisted essentially of an exhauster operated by compressed air which drew air from the surroundings through a Soxhlet thimble, thus filtering it. The entry duct to the Soxhlet thimble was of fairly large dimensions to increase the volume of dust laiden air inducted into the collector. It was found, so far as could be established in the samples obtained, that the Soxhlet thimble stopped even the finest of particles which can be seen under the optical microscope, i.e. $\leq 0{\cdot}5\mu$, from passing into the compressed air line. Fig 1 is a schematic drawing of the H-J dust collector.

Compressed air was chosen to provide suction since service trunking carrying compressed air, usually at about 50 lb./in^2, is to be found near most coal faces where it is provided to operate various pieces of coal-mining equipment. At the time of production of the prototype the collector was of unique design, but since then a collector of similar design known as the Hexhlet dust-sampler has been produced commercially by Messrs. Casella (4) from a design by Wright (5).

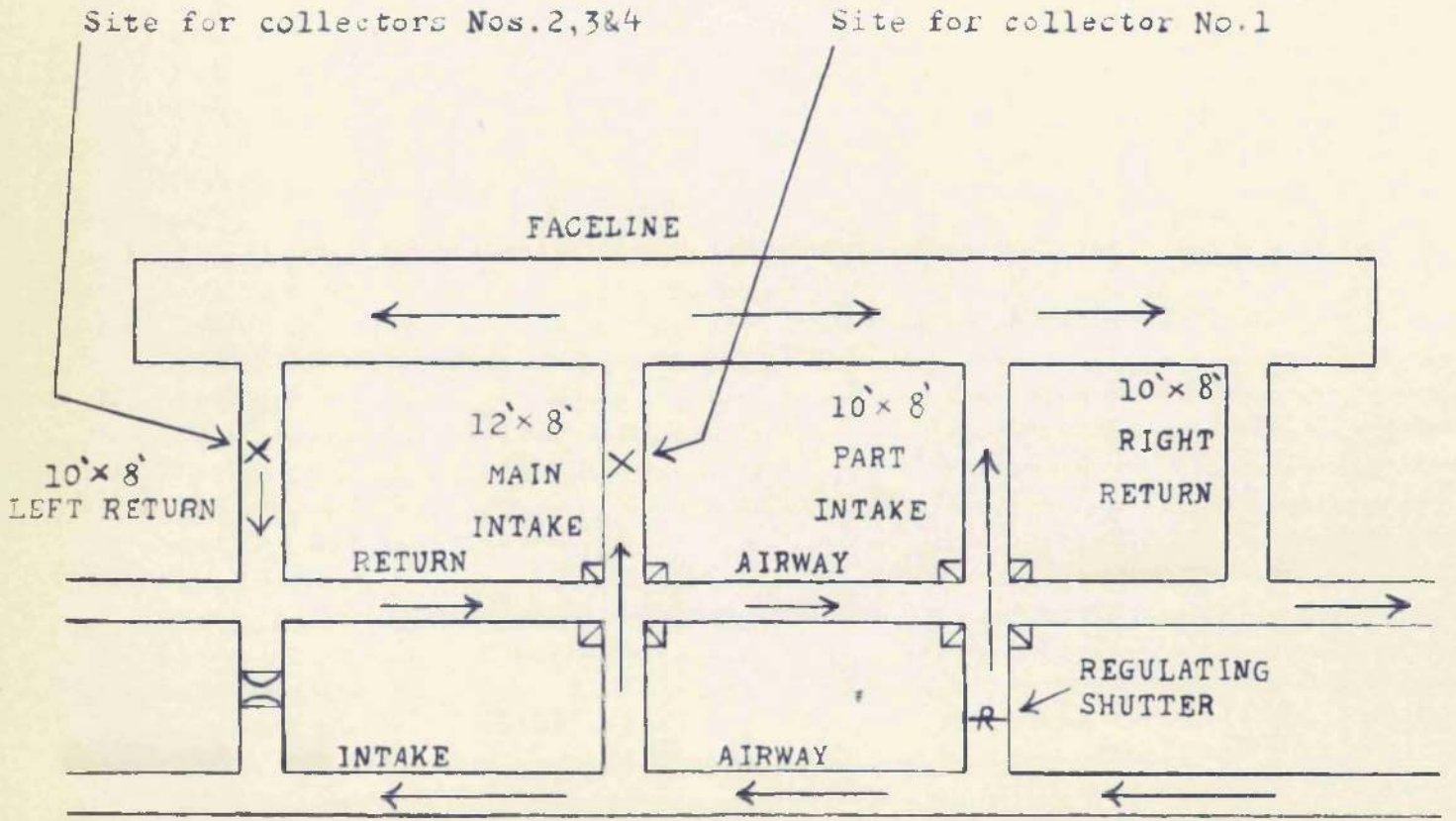
Operation of Collector in Pit

Since dust concentrations sufficiently high to create a serious health hazard generally occur only near the working face in present day collieries, the collector was invariably operated between 20 yd. and 50 yd. from the face, usually in one of the return airways. At such a distance from the face i.e. greater than ten effective roadway diameters, the dust concentration is reasonably uniform over the cross-section of the roadway and there is no appreciable change,

Fig 2

Sketch Plan of Collector Situation Underground

(Arrows show direction of airflow)



due to deposition, in the concentration of dust of respirable size (6).

Fig 2 shows how four samplers were arranged to collect airborne dust samples in Cordowan No. 1 Pit, No. 2 East Section. No. 1 sampler was positioned as indicated in the Main Intake Road 75 ft. from the faceline and sampled the intake dust continuously; Nos. 2, 3 and 4 samplers were positioned as indicated in the Left Return Road 75 ft. from the faceline. No. 2 sampler operated intermittently and collected the dust generated during the stripping shift for consecutive periods of eight hours duration, Nos. 3 and 4 samplers collected the dust generated during the brushing and cutting shifts on a similar basis. This period of sampling was carried out over six working days and represents a typical underground dust collection programme.

It should be noted that a series of point sources along the face were responsible for the dust cloud in the return, so that the dust produced from any given source was mixed longitudinally by an amount depending on its position with respect to the sampling point. Any appreciable changes in longitudinal mixing in the return will only be produced, therefore, by workers near the return end of the face and these will be superimposed on a relatively large and slowly changing background. Further if the air flow in the roadways was turbulent, as was almost invariably so, the collector was sufficiently removed from the source for the dust concentration to be substantially uniform over the cross-section and sufficiently near to the source for there to be no appreciable loss of dust of respirable size due to deposition.

Efficiency of Collector

The rate at which the H-J Sampler collects dust, apart from the efficiency of the equipment itself, is obviously dependent upon the pressure of the compressed air fed to the exhauster and the concentration and average particle diameter of the dust cloud sampled.

Various other factors such as the density of the dust being collected and the viscosity and density of the gas being filtered will also influence the rate of collection, presumably to a lesser degree; but proper assessment of these factors under the very variable conditions at the coal face was thought not to be practicable.

Seven runs were performed, however, under reasonably standard conditions, and an estimate of the collector's efficiency was attempted from the results obtained from these runs, which are tabulated in Table 1. The samples from which these data were derived were the four collected in the exercise mentioned previously, and a further three samples collected in the Return Road at No. 7 Section of Kingshill No. 3 Colliery during the cutting, stripping, and brushing shifts. The compressed air pressure during collection of these samples was substantially constant at around 50 lb./in.^{2}.

The figures given for dust concentration (C) are expressed in particles per cubic centimetre. These concentrations were determined from thermal precipitator surveys carried out by National Coal Board samplers during the period of collection and represent the concentration of dust in the 1 to 5 μ particle size range expressed as a mean for the period, this mean being determined from many estimations. The average particle size (D) was calculated from particle size analysis of a thermal precipitator slide which represented, as nearly as possible, the mean concentration of the dust during the period of collection. To be consistent with the units in which dust concentration is expressed (7), D was calculated as

$$D = \sqrt[3]{\frac{\Sigma n d^3}{\Sigma n}} \qquad \text{----------(1)}$$

where n = number of particles counted in a given size range

d = mean projected diameter of particles in given size range.

Application of the usual filtration formulae to the problem of explaining the results obtained proved unsuccessful, but the following formula, which is derived purely from examination of experimental data of the type given in Table 1, is suggested for making a rough preliminary estimate of the order of time required to collect a given weight of dust under known conditions of mean dust concentration and of mean particle size, namely,

$$\log_{10} T = (\log_{10} W + 2.342) - (0.753 \times 10^{-4} \times CD^3) \quad \text{------ (2)}$$

where W = weight of colliery dust collected in grams.

C = mean dust concentration (1 - 5u) in particles per cubic centimetre.

D = average particle size, as derived from equation (1) in microns

T = time of collection in hours

This empirical relationship enables the time of collection to be roughly forecast only when the compressed air fed to the exhauster is at a pressure of approximately 50 lb./in^2.

Table 1

Collector Performance Data

Sample	Weight (W) g.	Collection Time (T) Hours	Dust Concentration (C) p.p. C.C.	Particle Size (D) -u
C.2	2.2	48	286	3.20
C.3	5.5	48	256	3.64
C.4	11.7	48	322	3.63
C.5	1.4	144	123	3.62
3.K.3	1.2	120	164	2.35
3.K.4	2.5	120	381	2.97
3.K.5	2.5	90	272	4.05

Thus, according to equation (2), in order to collect 5.0 grams of airborne colliery dust having an average particle size D, of 3.0 μ under a mean dust concentration (1 to 5 μ) of 300 particles per cubic centimetre it would be necessary to operate the collector underground for a period of approximately 275 hours. While this is only an approximate estimate of the time necessary to collect 5.0 grams of airborne dust under the conditions exemplified, the result shows that the collection of large amounts of airborne dust using this type of macro-sampler is inevitably lengthy and consequently expensive.

As a rough check on whether the Soxhlet filter was allowing small dust particles to pass and thus leading to preferential filtration, particularly during the first few minutes of samplings before a secondary filter of collected dust had formed, a Soxhlet thimble in which a sample had been collected was scraped clean with a spatula, washed with water, dried, weighed and finally ignited in a muffle furnace at 750°C. The ash content of the thimble (0.41%) could be attributed to the coal dust still adhering to the thimble after washing. It is therefore probable that no preferential filtration is taking place, since, if this occurred, a deposition of some finely divided mineral material would be expected in the pores of the thimble; and this is evidently absent.

Conclusion

While the H-J macro dust sampler inevitably requires long collection periods underground in order to obtain useful quantities of airborne dust, it appears to be efficient in collecting even the smallest airborne particles.

PARTICLE SIZE DETERMINATION BY OPTICAL MICROSCOPY

Instrumentation

One of the most important factors affecting the health hazard of a dust cloud is the size of the dust particles, since only very small particles can penetrate to the terminal air sacs of the lung. The most direct method of estimating the size is to view the dust, in a suitably dispersed form, by means of a calibrated microscope.

The instrument employed in the present investigation was a Vickers (8) projection miscroscope with a 4 mm. achromatic objective, which was essentially a normal compound microscope with the lens system inverted so that the stage was uppermost. The image from the eyepiece was projected by means of a plane mirror on to a ground glass screen for final viewing or photographings, thus rendering particle size counts much less tedious than with a normal compound microscope. Light was transmitted from source to objective via a condenser, concave mirror and adjustable iris, and a parabaloid condenser gave dark field illumination with objectives of 4 mm. and greater focal length. The stage was also fitted with two screw adjustments so that the field could be traversed in any direction. The light source was originally a carbon arc lamp, but this was later replaced by a mercury vapour lamp and ultra-violet filter.

When performing dust counts a X10 Huygens eyepiece incorporating a graticule was used, a development of that described by Paterson and Cawood (9). This consisted of a central rectangle subdivided into nine smaller rectangles and having along the top and bottom a series of graduated circles (the set on the bottom being outlined and that on the top being darkened) arranged in a $\sqrt{2}$ progression. The image of this graticule was naturally projected on the viewing screen together with the image of the dispersed dust, and the size of each dust particle within the large rectangle was estimated by comparison of its projected diameter on the longer side of the rectangle, with

the diameters of the circles on the graticule. In this way the particles were divided into various size ranges, and a size range-frequency distribution obtained. Dark field illumination to prevent errors due to the presence of haloes of light around the dust particles, created by diffraction of the incident light on the specimen, was normally employed using a 4 mm. objective, which with a X10 eyepiece gave a magnification of 1,055 and a graticule range of approximately 0.7 μ to 12.7 μ. The graticule was calibrated, before particle size analysis using a stage micrometer.

Counting and Dispersion Errors.

Apart from errors in sampling., which affect all methods of size analysis, inaccuracies are encountered when sizings microscopically owing to incomplete redispersion of the dust sample on the slide, the counting of an insufficient number of particles and inaccurate estimation of the size of non-spherical particles from their projected diameters. The first two causes will be dealt with below at some length, but it is sufficient to say of the third cause, for the purposes of this work, that a shape factor is required to correlate the results obtained from microscopic analysis with those obtained from falling speed methods (9).

The size range-frequency data thus obtained from the various dust samples were converted to a mass-frequency basis, on the assumption that all particles were of the same density. This is obviously invalid for a heterogeneous powder such as airborne colliery dust, but it is approximately correct, and on this basis :

$$\text{Percentage in Grade by weight} = \frac{n d^3}{\Sigma n d^3} \quad \text{- - - - - - - - - - (3)}$$

where n = number of particles counted in grade

d = mean projected diameter of particles in grade

Thus by multiplying the number of particles in each size grade by the cube of the mean projected diameter a mass percentage undersize curve for each sample can be constructed.

Obviously large errors in these curves may be incurred through counting too few particles. Table 2 gives a summary of results (9) for the probable error incurred when counting particles in a given size range, with successive ranges in $\sqrt{2}$ ratio. The results quoted in Table 2, it must be remembered, only forecast the error due to statistical causes, and complete redispersion of the dust is of course assumed, with dust particles all of equal density.

Table 2

Number of Particles to Count for a Specified Accuracy

Estimated percentage in grade by weight	Probable Error 1%		Probable Error 2%	
	Upper & lower % limits in grade	No.of particles to count for accuracy within 1%	Upper & Lower % limits in grade	No.of particles to count for accuracy within 2%
5	4 - 6	25	3 - 7	6
10	9 - 11	100	8 - 12	25
15	14 - 16	225	13 - 17	56
20	19 - 21	400	18 - 22	100
25	24 - 26	625	23 - 27	156
30	29 - 31	900	28 - 32	225
40	39 - 41	1600	38 - 42	400

In the present dust counts between 600 and 800 particles were normally sized and mass percentage undersize curves were drawn from these data. From these curves the percentage mass of the dust cloud below 5 μ in size (i.e. "respirable dust") was derived for each sample and these data are given in the final section of the thesis. The accuracy of these figures, due to statistical errors, can be estimated from Table 2, and the probable error due to counting inaccuracies is normally only between 1% and 2%

Redispersion of a dust in exactly the same way as it was originally dispersed is virtually impossible for various reasons and some dispersion error is thus inevitable if the collected dust is to be subjected to microscopic particle size analysis. In determining a size distribution the problem is first to obtain a complete and homogeneous dispersion of the dust sample and then to transfer a suitable portion of this to a microscopic slide or cover glass for examination. If a liquid is used as dispersion medium, difficulties due to segregation of coarse particles on account of their more rapid sedimentation are encountered if a non-viscous liquid is employed, while by using a viscous liquid it is difficult to avoid some degree of agglommeration since particles, particularly fine particles, tend to stick together. A compromise is the best which can be achieved under these conditions and with this end in view it was decided to investigate three of the best methods of dispersion used by previous workers, to discover which was most effective for use in these investigations. It was decided that the dispersion method which resulted in the greatest proportion of fines could be taken as the most effective.

The three methods of dispersion described below were carried out on airborne dust sample 3.K.1.

(i) About 0.1 g. of the airborne dust sample was placed at the bottom of a glass tube, 2 in. in diameter and 12 in. in length, drawn to a narrow

opening at the bottom. A thermal precipitator head was fitted to the top of the tube and a rubber bulb was connected to a narrow opening at the bottom. A sharp puff of air was then blown into the tube thus dispersing the dust and 100 cc. of the resulting aerosol was aspirated through the thermal precipitator. The cover glasses were removed from the thermal precipitator head and fixed to a clean microscope slide using a thin film of nail varnish around the rim to prevent contamination by atmospheric dust.

The thermal precipitator (4) is the standard instrument employed in British coal mines for airborne dust assessment by optical microscopy. Its action depends on the repulsion of airborne dust by a heated body due to differential molecular bombardment in a thermal gradient.

When assessing the density of a given dust cloud, a measured volume of dust-laden air is drawn at about 7 cc. per minute through a narrow channel across which is a heated wire, energised by a small portable accumulator, the volume being measured by a simple displacement aspirator. Samples for optical counting are collected on two cover glasses mounted on opposite sides of the wire, the dust deposits forming a strip about 1 mm. wide and 10 mm. long across a diameter of the cover glasses. These deposits may readily be counted under an optical miscroscope.

(ii) 5 ml. of a stock 10% solution of ethyl cellulose in toluene (9) was diluted with an equal volume of toluene and heated in a small beaker on a water bath. About 0.1 g. of the airborne dust sample was added and the mixture was allowed to cool with stirring. A drop was then removed from the mixture with a glass rod and placed on a clean cover glass, which was then mounted on a slide for examination in the above manner. Eight cover glasses were prepared in this way and the best two were chosen for the complete size analysis count.

(iii) About 10 ml. of redistilled n - butyl alcohol was placed in a

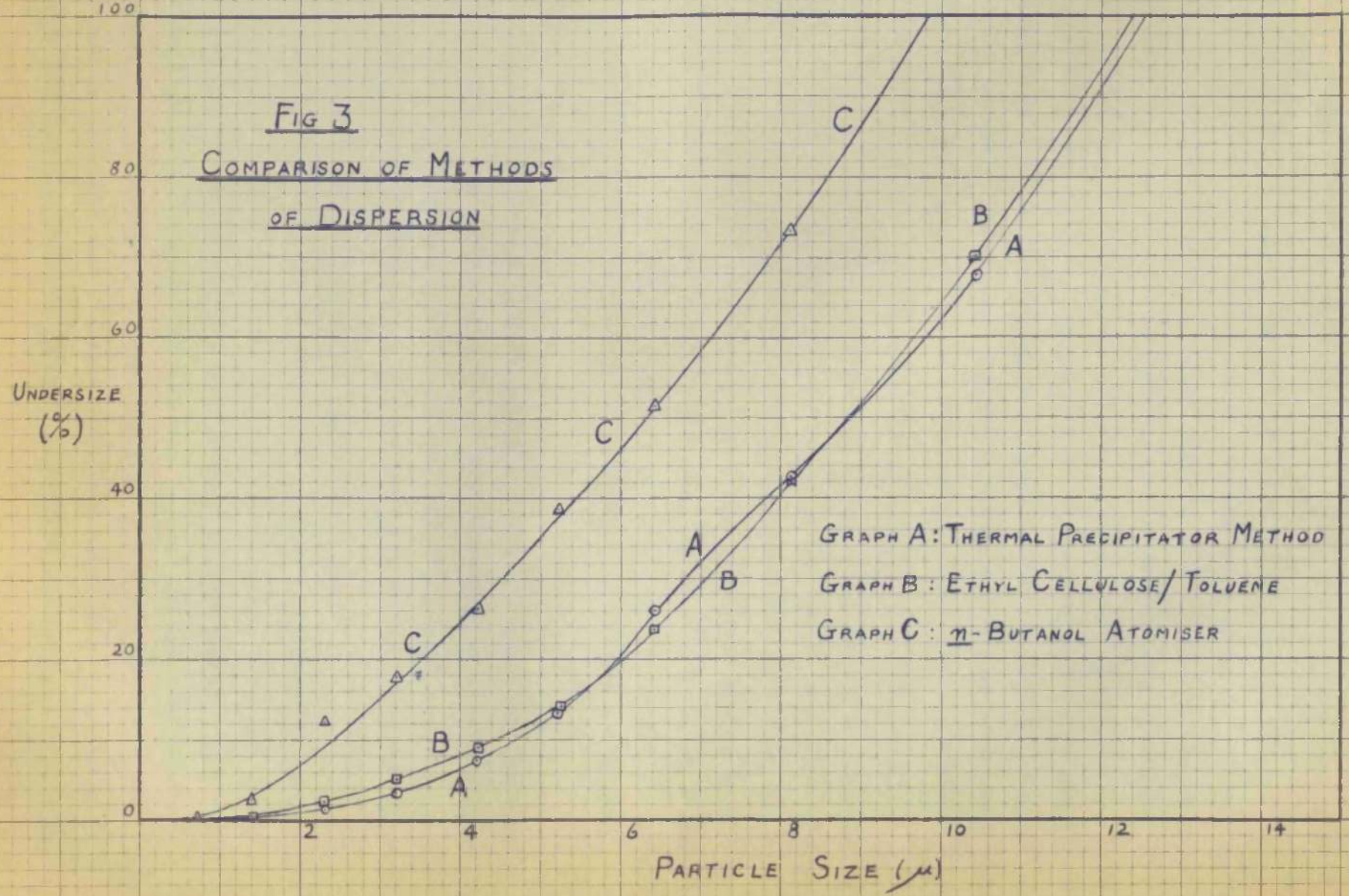


FIG 3
COMPARISON OF METHODS OF DISPERSION
UNDERSIZE (%)
100
80
60
40
20
0
2
4
6
8
10
12
14
PARTICLE SIZE (μ)
C
B
A
GRAPH A: THERMAL PRECIPITATOR METHOD
GRAPH B: ETHYL CELLULOSE/TOLUENE
GRAPH C: n-BUTANOL ATOMISER

small glass atomiser, fashioned in the manner of a scent spray, and about 0.1 g. of the airborne dust sample was added to the liquid, which was then swirled around to disperse the dust. The mixture was then sprayed on to a clean cover glass propped at an angle against a hotplate. Eight cover glasses were prepared in this way and mounted on slides and the best two were chosen for the final examination.

The result of the size analyses of this one dust sample dispersed in these three different ways is shown in Fig 3 in the form of percentage mass undersize curves. It will be noted that the slides which were obtained from an atomised n - butyl alcohol suspension of the dust contain the largest proportion of fines. It can be taken that this method of dispersion is therefore the best of the three methods investigated and it was consequently adopted for both optical and electron microscopy.

In the above size analyses the particles were divided into ten graticule groups having average particle sizes in the range 0.7 μ to 12.7 μ, but, in view of the considerable number of particles having a projected diameter of greater than 12.7 μ, it was found necessary in many later cases to measure these large particles individually using a paper scale and to allow for them in the analyses, since one or two large particles can, naturally, have a much greater effect upon the percentage mass undersize curve than many small particles.

It is now necessary to know how exactly airborne dust redispersed by the atomiser technique described above represents the original dust cloud from which the sample was obtained.

The error to be expected from such redispersion was therefore estimated using a number of shift samples obtained from Kingshill No. 3 and Cardowan Collieries, where thermal precipitator samples had been taken by National Coal Board samplers every half hour throughout the collection period at the site of the collector. From these thermal precipitator samples the concentrations of the dust clouds in terms of particles

per cc. in the ranges 0.5 to 5 μ and 1 to 5 μ were estimated by N.C.B. workers by miscroscopic dust counts (10) (11) and the mean concentration of the dust cloud during sampling was thus calculated. Thermal precipitator slides as nearly as possible representative of the mean dust concentration during collection were chosen for comparison with the redispersed dust.

In only four cases was sufficient dust available to make a comparison using the atomiser method as described above, although, in a fifth case (3.K.5), only about 0.01 g. of the dust sample was sprayed on to a cover slip as before. The size distributions obtained were used, firstly to construct percentage mass undersize curves in the usual way, from which the percentage mass of less than 5 μ could be read off, and secondly to calculate the value of the average particle diameter d_3 from the relationship.

$$d_3 = \frac{\Sigma N d^3}{\Sigma N d^2} \quad \text{----------} \quad (4)$$

These data were used to compare the size distributions obtained on microscopic examination of the thermal precipitator samples and the redispersed dust as shown in Table 3.

Table 3

Effect of Re-dispersing Dust

(i) Comparison of Mass % < 5 μ

Sample	C.2	C.3	C.4	3.K.4	3.K.5
Result obtained using thermal precipitator slide	30.7	18.8	30.1	56.3	22.5
Result obtained using slide with redispersed dust	10.1	9.2	8.2	10.8	17.9

(ii) Comparison of d_3 Values

Sample	C.2	C.3	C.4	3.K.4	3.K.5
Result obtained using thermal precipitator slide	6.6	6.4	5.9	4.2	6.9
Result obtained using slide with redispersed dust	9.9	10.4	10.2	9.3	7.4

It will be seen that there is a large and variable difference between the results, and although closer agreement between the results is show for sample 3.K.5 than in any of the others, the more dilute suspension employed here in preparing the slides could not have been generally employed, since it led to increased difficulty in obtaining a slide of suitable optical density, free from significant contamination from atmosphere dust.

There are three possible causes of this variation between the result for a sample taken from the original dust cloud and that for a redispersed dust. These are (i) a dispersion error due to incomplete redispersion by the atomiser resulting in the presence of some aggregates of dust on the slide, (ii) failure of the thermal precipitator to collect large particles and (iii) failure of the dust collector to collect small particles.

A thermal precipitator sampling under isokinetic conditions is known to have an efficiency of 100% at a particle size of 5-μ (12) an apparent efficiency of 110% at a particle size of 10-μ, owing to the greater tendency of large particles to be aspirated into the air stream through the thermal precipitator, and an efficiency of 75% at 20-μ, owing to the lesser tendency of large particles to be deposited by the thermal gradient. To ascertain, therefore, whether the variation between the results was due mainly to the varying efficiency of the thermal precipitator with particle size, or to a dispersion error, the number

of particles counted in a particular size fraction of the redispersed dust, say N_D, was compared with the particles counted in the same fraction on the thermal precipitator slide, say No. The average value of the ratio N_D/No for the five samples concerned was calculated for three different size fractions and compared with the value of N_D/No to be expected owing to variation in thermal precipitator efficiency alone.

Table 4

Particle Size (u)	Value of N_D/No to be expected due to varying T.P. efficiency	Average value of N_D/No obtained
5.2	0	- 0,074
10.4	- 0.991	+ 2.84
18.4	+ 0.333	+ 00

It is seen that the variation between corresponding size fractions of the redispersed and original dust is much greater than that expected from thermal precipitator inaccuracies alone. Further, since the variation is not confined to small particles, but, in fact, increases with particle size, it is reasonable to conclude that the observed variation is due not primarily to failure of the dust collector to collect small particles, but almost entirely to inability to redisperse the collected dust effectually.

Instrumental Errors

It was noted, on comparison with typical National Coal Board dust counts, that the first five airborne coal dust samples examined under the Vickers microscope showed an unusually small proportion of particles in the 0.5 to 1-u range.

The dust counts in question were performed on slides which had been prepared by redispersing the dust by the usual spraying technique and, as shown above, a considerable dispersion error would therefore be associated with the count. However, in order to investigate whether an instrumental error was also involved, the same slides were counted by National Coal Board workers at Shotts Laboratories (13) using the normal Beck microscope employed by the Board. The Beck instrument, as used for normal dust counts, is fitted with a 2 mm oil immersion apochromatic objective and the final image is projected on to an opaque external screen, the source of illumination being a mercury vapour lamp. In the Vickers instrument, on the other hand, a carbon arc was used as the source of illumination and a 4 mm achromatic objective was employed, the final image being projected on to a ground glass screen. An approximate size distribution was also obtained from a number of electronmicrographs prepared from each sample.

The results for the number and mass percentages of less than 1 μ size shown in Table 5 demonstrate clearly since the results for the Beck and Vickers microscopes were obtained using the same slides, that the resolution of the Vickers instrument using a 4 mm objective and ground glass screen was too low to enable the 0.5 to 1 μ fraction to be properly detected. Further, while the number of particles which could be counted on the electronmicrographs (70 to 260) was too small for an accurate size analysis, the generally higher level of the approximate results again indicate the low resolution of the Vickers instrument.

Table 5

Comparison of Microscopes

(i) Comparison of Number % of $< 1\mu$ Fractions

Sample	Microscope used		
	Vickers	Beck	Electron
3.K.1	19.0	37.5	47.9
C.1	13.8	69.2	53.8
3.K.2	9.0	63.4	51.1
1.K.1	8.0	57.9	51.3
L.V.1	11.0	68.2	47.7

Table 8 (continued)

(ii) Comparison of Mass % $< 1\mu$ Fractions

Sample	Microscope used		
	Vickers	Beck	Electron
3.K.1	0.2	0.3	1.4
C.1	0.1	0.3	0.2
3.K.2	0.1	0.3	0.9
1.K.1	0.1	0.3	1.4
L.V.1	0.1	0.4	1.1

Fitting a 2 mm oil immersion objective to the Vickers microscope and replacing the carbon arc lamp with a mercury vapour lamp enabled

the 0.5 to 1 μ fraction to be accurately estimated. This alteration also resulted in the graticule range becoming too small to enable adequate counts on the mass basis to be made over the entire range of particle size present however, and resulted in a considerable increase in the tedium of counting as dark field illumination could no longer be employed.

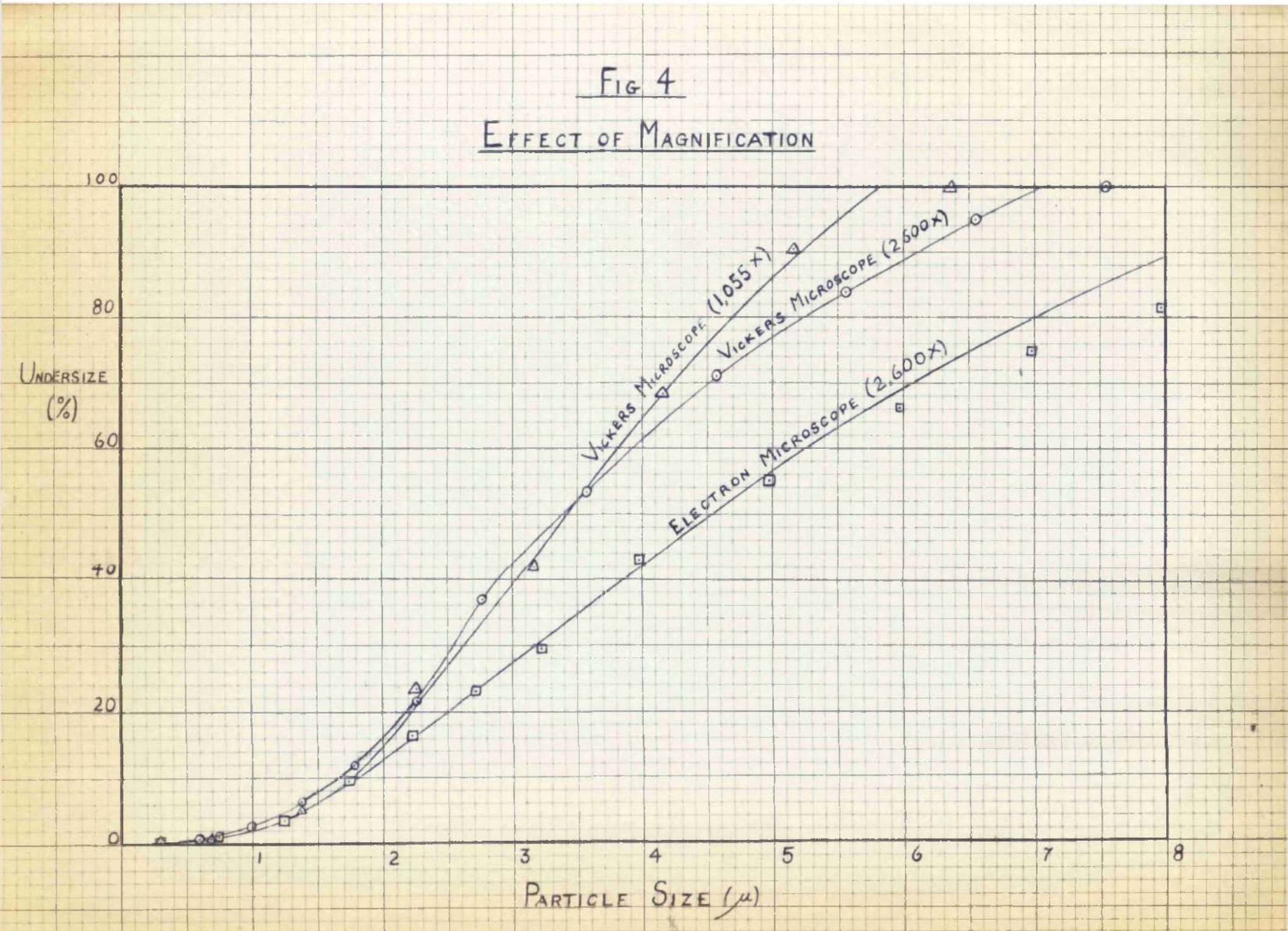
It was therefore decided to use the slides obtained by the National Coal Board in their thermal precipitator surveys made while the collector was in operation. In this way any errors due to failure of the sampler to collect fine particles or to incomplete redispersion of the dust on the slide are avoided, and the correct number fraction between 0.5 and 1.0 μ can be estimated using mean dust concentration figures. These figures are calculated from counts performed using the Beck microscope as described with an N.C.B. graticule by means of which the particles viewed are divided into four size groups, namely, $< 0.5\,\mu$, 0.5 to 1 μ, 1 to 5 μ, and $> 5\,\mu$. The fractions of $< 0.5\,\mu$ and $> 5\,\mu$ are not counted and the mean dust concentrations calculated from the counts are expressed as particles per cc. in the ranges 0.5 to 5 μ and 1 to 5 μ.

Since the N.C.B. graticule is not suitable for the detailed size analysis necessary to obtain an accurate mass ratio distribution, it was decided to count typical slides for each sample on the Vickers microscope and to calculate the mass distribution therefrom, since on the mass basis errors in counting the 0.5 to 1.0 μ fraction have very little effect. The correct mass fraction from 0.5 to 1.0 μ can then be estimated by substituting the number fraction obtained from the N.C.B. figures in the usual expression for the mass ratio, shown in equation (3).

In order to test the submission that the mass distribution obtained on analysis was not seriously affected by the drop in magnification the

Fig 4

Effect of Magnification



effect of varying magnification upon the values obtained for the percentage mass of less than 5μ and for the average particle size d_3 was studied, using commercial silica dust ("D.R.C. grade"). The dust was suspended in redistilled n - butyl alcohol and sprayed on to a slide using an atomiser in the usual way. Eight slides were thus prepared and the best was examined under a Vickers microscope, first employing a 4 mm objective and then a 2 mm oil-immersion objective. The dust was then similarly dispersed upon a collodion-covered grid-plate and examined under an electron microscope. The results obtained are shown in Table 6 and in Fig 4.

Table 6

Effect of Magnification

Instrument Employed	Magnification	No. of particles counted	Mass % < 5μ	d_3
Vickers	1,055	669	85.5	3.33
Vickers	2,500	1205	76.2	3.16
Electron	2,600	656	52.2	3.86

It will be seen that, using the Vickers instrument, increasing the magnifying power of the microscope beyond 1,000 X does not affect the values of either the percentage mass of less than 5μ size or the average particle size d_3 within the limits of experimental error. It is also seen that the increased resolving power of the electron microscope is more than counteracted by the inferior dispersion of the dust upon the collodion-covered grid of this instrument. Signs of agglomeration were very apparent in the electronmicrographs obtained.

FIG 5

SIZE ANALYSIS BY MASS: CARDOWAN CUTTING SHIFT

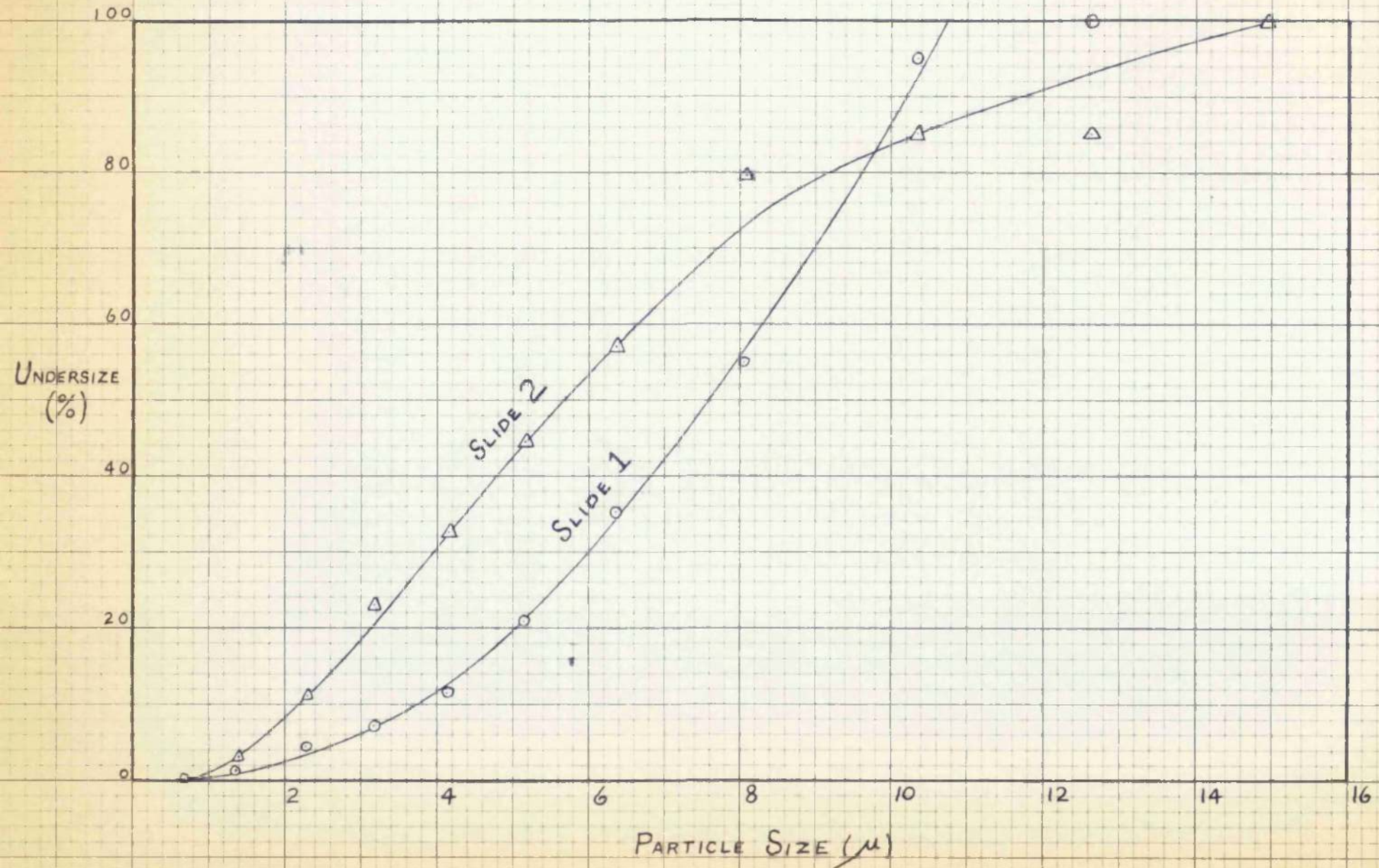


FIG 6

SIZE ANALYSIS BY MASS: CARDOWAN STRIPPING SHIFT

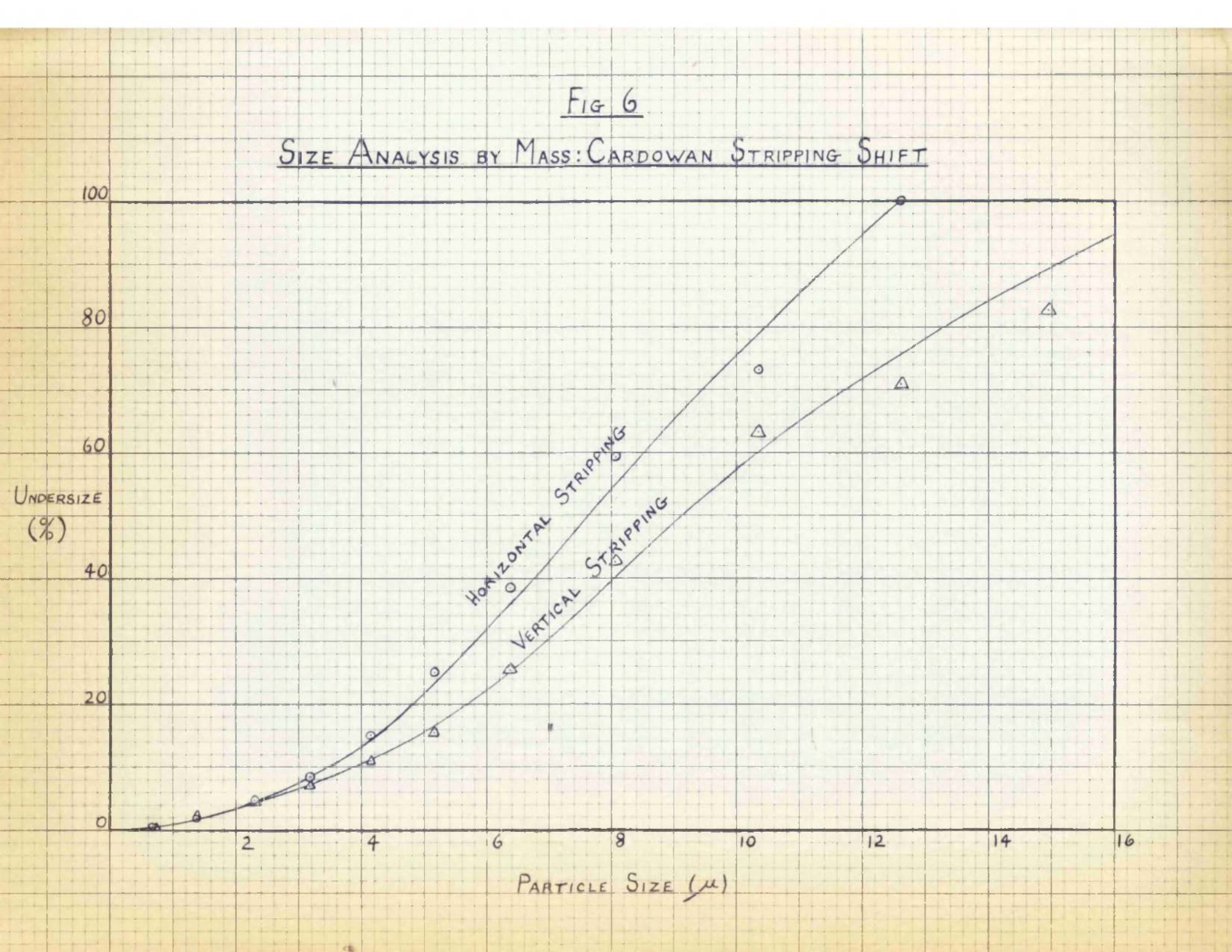


Fig 7

Size Analysis by Mass: Cardowan Brushing Shift

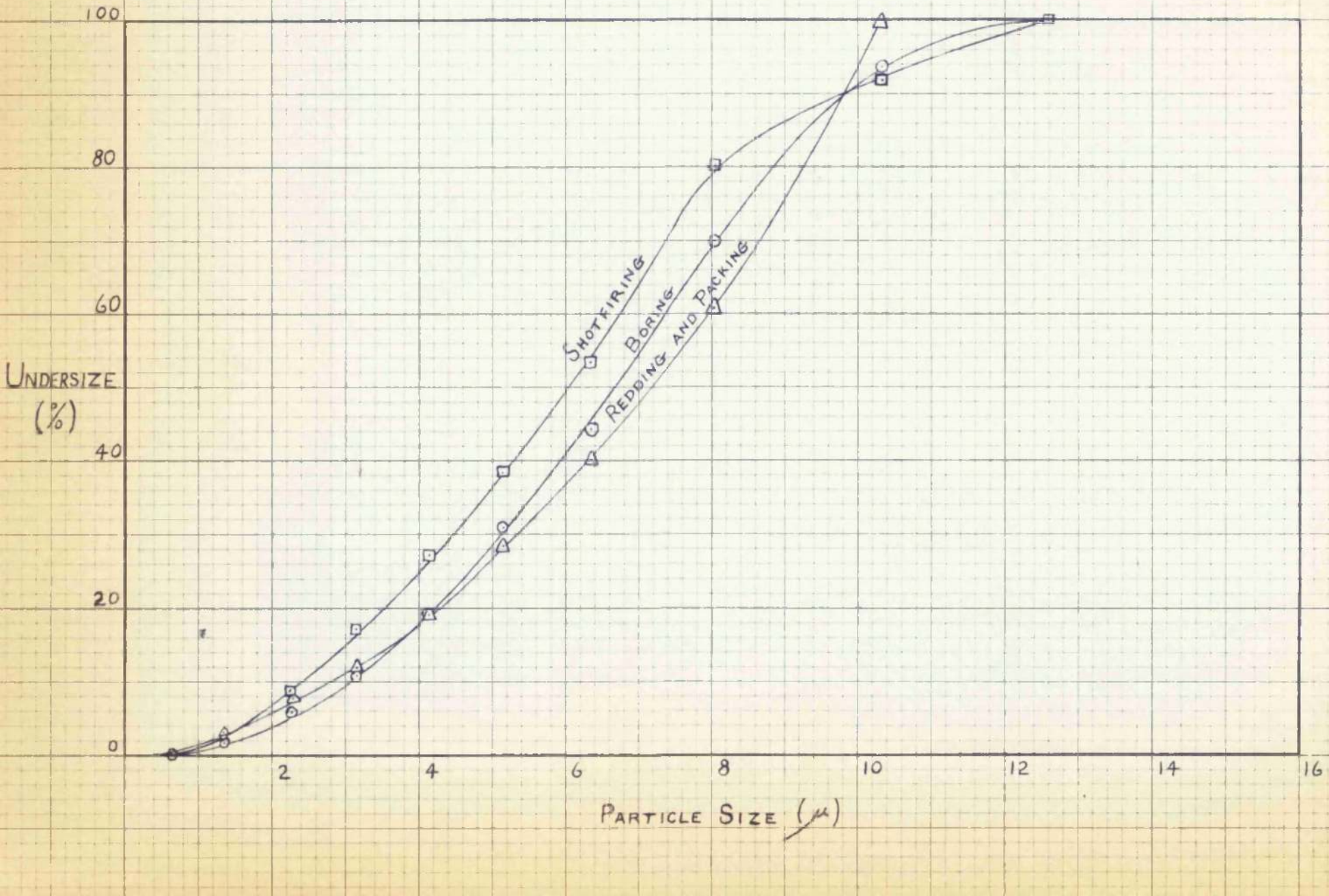


Fig 8

Size Analysis by Mass: Cardowan Intake Road

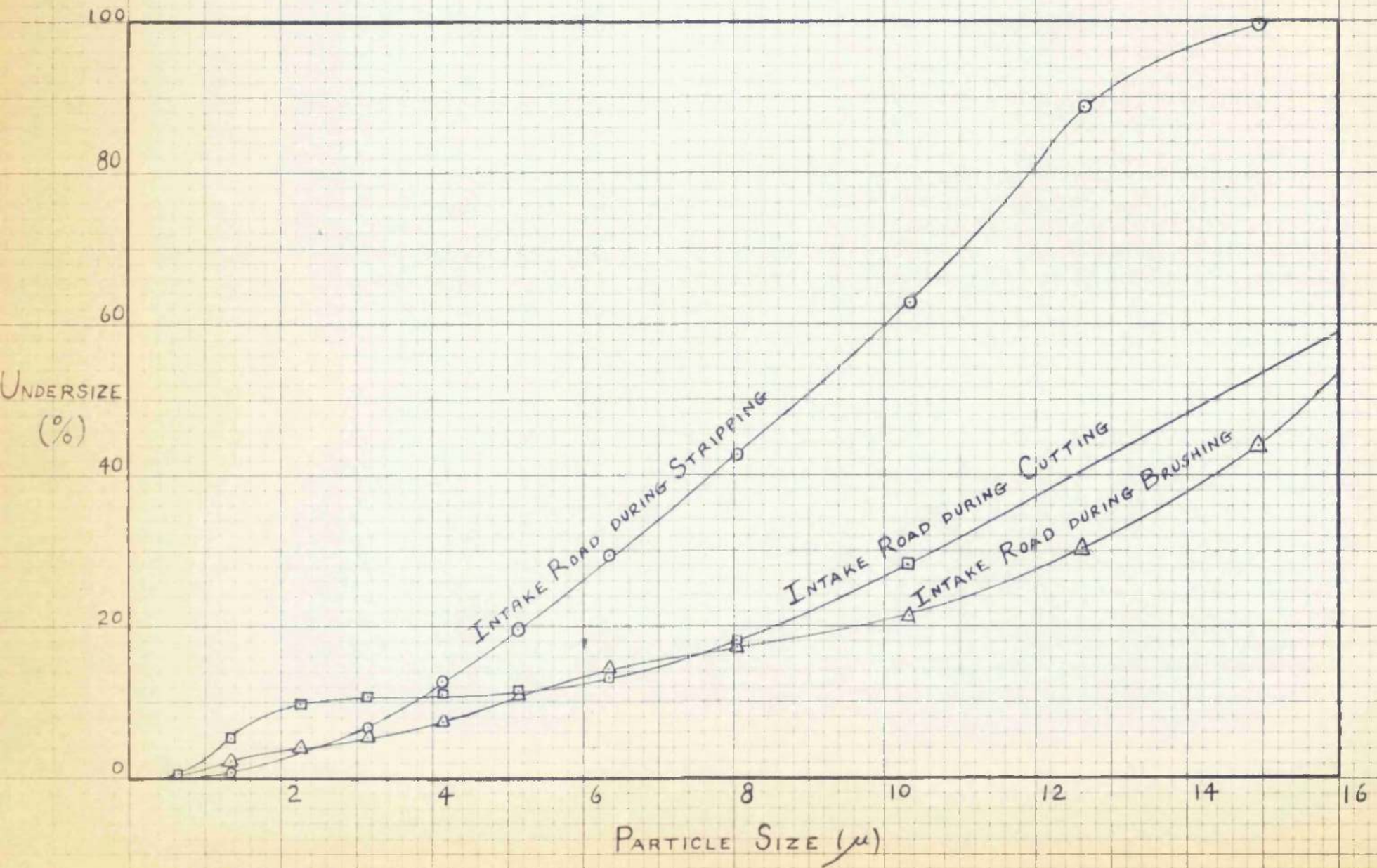
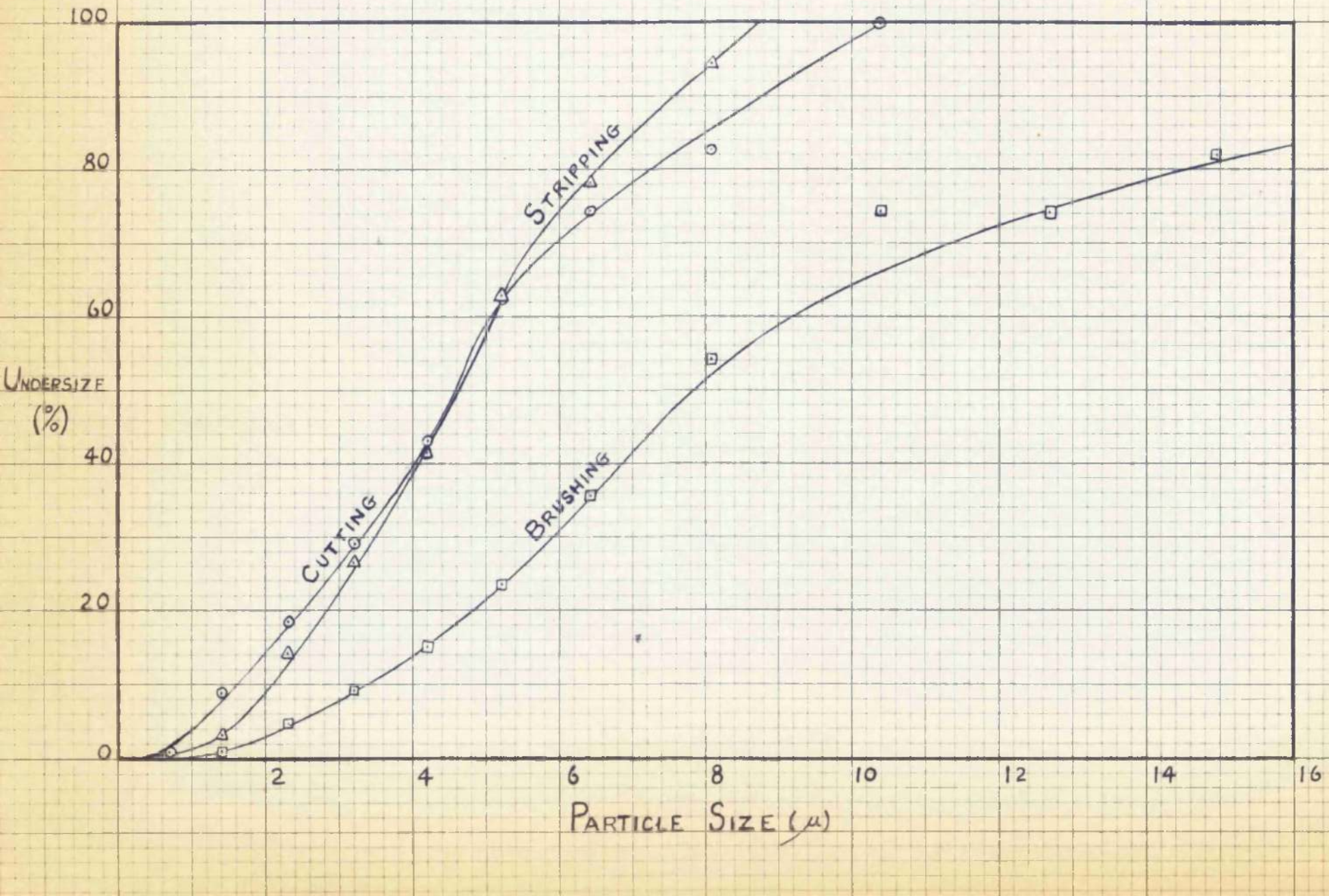


FIG. 9

SIZE ANALYSIS BY MASS: KINGSHILL No. 3 SHIFT SAMPLES



Sampling Errors

As mentioned above it was decided to use thermal precipitator slides obtained from the actual dust cloud sampled, when available, for examination under the optical microscope and subsequent particle size analysis.

While this procedure eliminates the large error inherent in redispersing the dust, it can also lead to the introduction of a serious sampling error in consequence of the variation of dust concentration and particle size distribution during the period of collection.

Figs 5 to 7 show the variation of particle size distribution of dust clouds sampled in a return airway in Cardowan Colliery throughout cutting stripping and brushing shifts. It will be seen that particle size distribution varies quite considerably during any one shift. This variation occurs whether or not the same mining operation is being carried on throughout the shift. Fig 8 shows that considerable variation in dust size distribution also take place in the intake airway, although here the percentage mass of dust particles of respirable size is consistently lower than in the return airway. Fig 9 shows the size distributions of dust clouds in a return airway of Kingshill No. 3 Colliery during each of the three shifts, obtained by analysis of slides chosen so that the counts agreed as nearly as possible with the mean dust concentration for the particular shift. It is seen that there is also a considerable variation in average size distribution from shift to shift.

Variations in dust concentration have been noted and measured by previous workers (6) who concluded that in order to determine an accurate figure for the mean dust concentration for a particular shift, a large number of samples must be taken during the shift and, similarly, in order to obtain a reliable estimate of the mean dust concentration for a number of shifts, it is necessary to sample over a large number of shifts. This, of course, results in a large number of thermal

precipitator samples being required, although the problem of establishing a reliable estimate for the mean concentration of airborne coal dust may possibly be overcome in the near future by the use of suitably calibrated automatic sampling instruments.

Similary, in order to establish an accurate average particle size distribution it is necessary to submit a large number of slides to detailed examination. This was not possible in the present work and a compromise was struck, in the case of later samples, by analysing two or three slides for each sample which were, as nearly as possible, representative of the average dust concentration during samplings.

Conclusions

A reasonably accurate estimate of the average particle size distribution of any dust cloud may be made provided, firstly that a sufficient number of thermal precipitator samples are taken underground at the point of collection to establish an accurate value for the mean dust concentration, and secondly that a sufficient number of particles are counted on a sufficient number of selected slides under an adequate optical system in sufficient detail to enable an accurate mass-basis analysis to be performed.

Since there appears to be no really effective method of redispersing collected airborne colliery dust, underground sampling by means of a thermal precipitator is necessary if an accurate result is required.

USE OF THE ELECTRON MICROSCOPE IN AIRBORNE DUST ASSESSMENT

General Principles of the Electron Microscope

In this instrument an electron beam has a function similar to that of a beam of light in an optical microscope and the final image is either recorded photographically or viewed by means of a fluorescent screen. The electron beam is produced by an electron gun similar to that used in a cathode ray tube and is propagated through the microscope body which must, of course, be under high vacuum. The lenses of the optical microscope are replaced in the case of the electron microscope by certain configurations of magnetic or electric fields which alter the path of the electron beam and form the final image. The final electron image is either projected on to a fluorescent screen where the electron energy is partly converted to light, making the image visible to the eye, or allowed to fall directly on a photographic plate to make a permanent record.

The instrument employed in this case was a Vickers type E.M. 3 microscope (14) which employs a condenser lens and three image forming lenses in analogy with the optical projection microscope.

The chief advantage of the electron microscope lies in its increased resolving power, which enables greater magnifications to be employed, and the increased resolving power is in turn dependent on the low equivalent wavelength of the electron beam employed.

The resolution limit of a microscope system is ultimately set by diffraction effects and may be defined as the least distance which can separate two minute object points which still remain separate in the final image. An arbitrary standard of the resolution limit, Δd, which closely agrees with observation, was suggested by Abbe who gave the limit as :

$$\Delta d = \frac{0.61 \lambda}{\sin \alpha} \qquad \text{----------} \quad (5)$$

where λ = wavelength of illuminating radiation in object space
α = half angle of the cone of illumination leaving one object point and passing through the objective lens.

For the optical microscope α may be nearly 90^{o} and λ, using ultra violet light, 2000 Å. Thus a limiting resolution approaching 0.1 μ may be achieved.

It was first postulated by de Broglie that a train of waves is associated with an electron in motion, the wavelength being given be :

$$\lambda_e = \sqrt{\frac{150}{V}} \qquad \text{----------} \quad (6)$$

where λ_e = equivalent wavelength in Ångstrom units
V = accelerating voltage.

Thus for electrons accelerated by 100 kV the equivalent wavelength of the illuminating radiation is approximately 0.04 Å and since owing to the aberrations in electron lenses, the aperture angle, α in equation (5), must be limited to approximately $\frac{1}{500}$ of that which can be used in the optical microscope, the theoretical resolution limit of the electron microscope is therefore about 5 Å, which is 200 times better than that of the optical microscope.

In practice such an improvement in resolution is not normally obtained, but the commercial electron microscope enables detail at least 20 times finer than that produced by the best optical microscope to be viewed and recorded.

Particle Size Determination

The importance of the fine dust particles smaller than 0.5 μ in diameter is not yet known. In order to assess their contribution to the health hazard of an airborne dust it is necessary to determine their relative surface and mass, and to find whether they are more or less toxic than the larger particles.

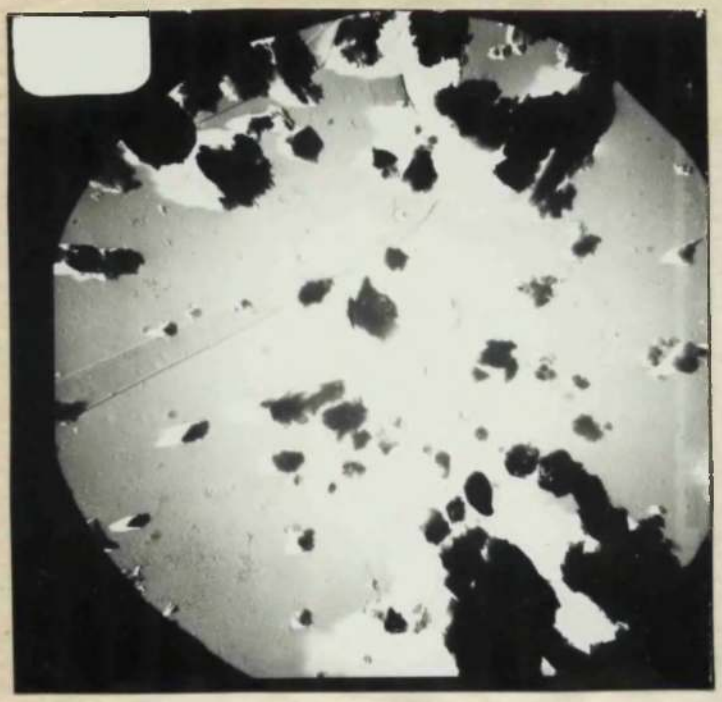


Plate 1
Airborne Coal Dust 3.K.1.
(2600 X)

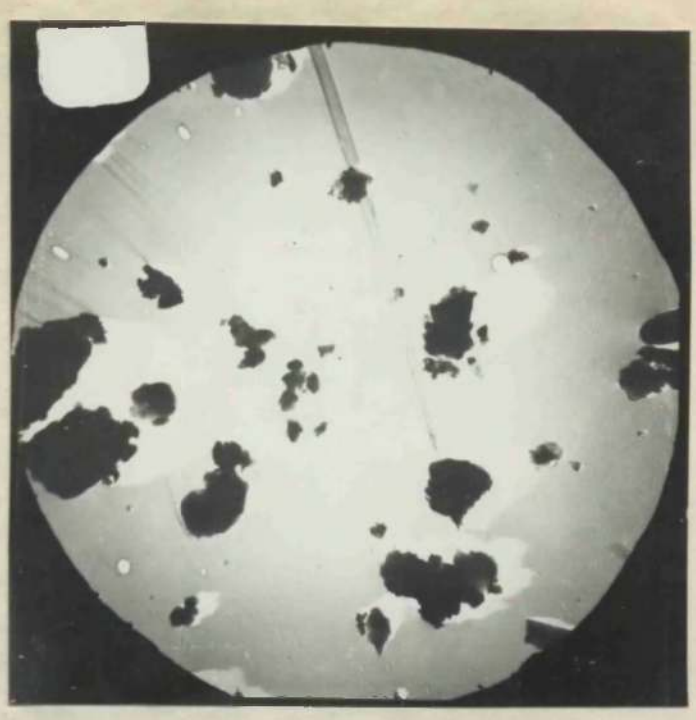


Plate 2
Airborne Coal Dust C.1.
(2600 X)

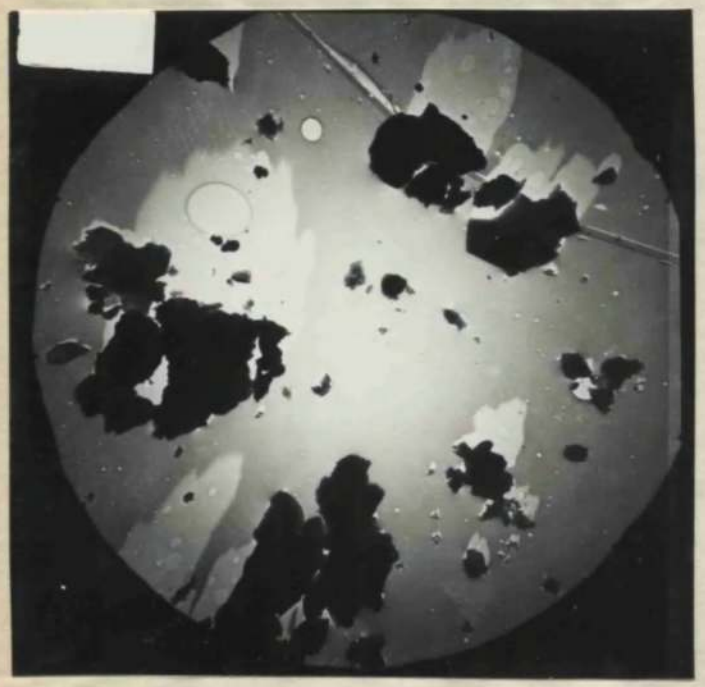


Plate 3
Airborne Coal Dust 3.K.2.
(2600 X)

Plate 4
Airborne Coal Dust 1.K.1.
(2600 X)

The electron microscope which is capable of resolving 0.01 μ details in routine operation is the only suitable instrument for such an investigation as the limiting resolution of an optical microscope, even under the best conditions is only about 0.3 μ. With this object in view therefore a large number of the airborne colliery dust samples collected were examined under the electron microscope.

About 0.1 g. of the dust under examination was dispersed in about 10ml. of pure n - butyl alcohol and sprayed in the manner described in the previous section on to a heated collodion covered specimen grid which was then mounted on the stage of the electron microscope and viewed under a magnification of 2,600 x using an accelerating voltage of 75 kV. Several electronmicrographs were then taken of each sample.

This limited treatment was insufficient to tackle the problem of estimating the proportion of particles of less than 0.3 μ in each sample, but to investigate this question fully would have been very expensive both in time and photographic materials, and insufficient resources were available for such a course.

Several interesting features were discovered however on examination of the electronmicrographs obtained, examples of which are shown in Plates 1 to 5. For instance the reason for the dispersion error described in the previous section is readily appreciated on examination of these plates as both small particles clinging to large particles and small particles adhering together in chainlike aggregates may be observed, and such aggregates would inevitably be recorded as single particles when viewed under the optical microscope. This effect is however slightly exaggerated in these plates as it is convenient to view a rather denser dust deposit under the electron microscope than under the optical microscope on account of the restricted field of view and stage motion of the former instrument. It was also possible to distinguish amorphous particles from crystalline particles in many cases, the former type of particles having frequently a cotton-wool like appearance

(Plate 1), while the latter type of particle had the sharp edges (Plate 2) characteristic of crystal growth or conchoidal fracture.

The quantitative investigation of the very small particles present in airborne dusts using the electron microscope does in fact involve a number of practical difficulties, chief among which is the problem of obtaining a sample of airborne dust in a suitable form for viewing which is free from errors due to segregation, or to redispersion, or to loss of dust in handling. However Cartwright and Skidmore (15) have shown how a thermal precipitator using membrane coated cover glasses may be used to overcome these difficulties and also that, using this technique, a reasonable fit is obtained, between the size analysis curves for a particular dust cloud using firstly an optical microscope and secondly an electron microscope provided that the lower limiting resolution and diffraction effects of the former instrument are allowed for. It appears therefore that, using the technique employed by the above, the problem of estimating the very small particles present in airborne colliery dust could be overcome if sufficient time and materials were available.

Electron Diffraction

Just as an interference pattern may be obtained using visible light and a diffraction grating on which the scratches are separated by a distance of the same order as the wavelength of the light, similarly an interference pattern may be obtained using an electron beam and a single crystal as diffraction grating, as the interatomic distances in the crystal are frequently of the same order as the equivalent wavelength of the incident electron beam. Such patterns may be obtained using the electron microscope type E.M.3 by means of suitable masking and focussing devices. If a regular interference pattern is obtained it is indicative of a regular or crystalline structure in the particle examined, while an amorphous particle, having a random type of structure, gives rise merely to a diffuse halo of light. Some idea of crystal size may also be obtained from these interference patterns as a single large

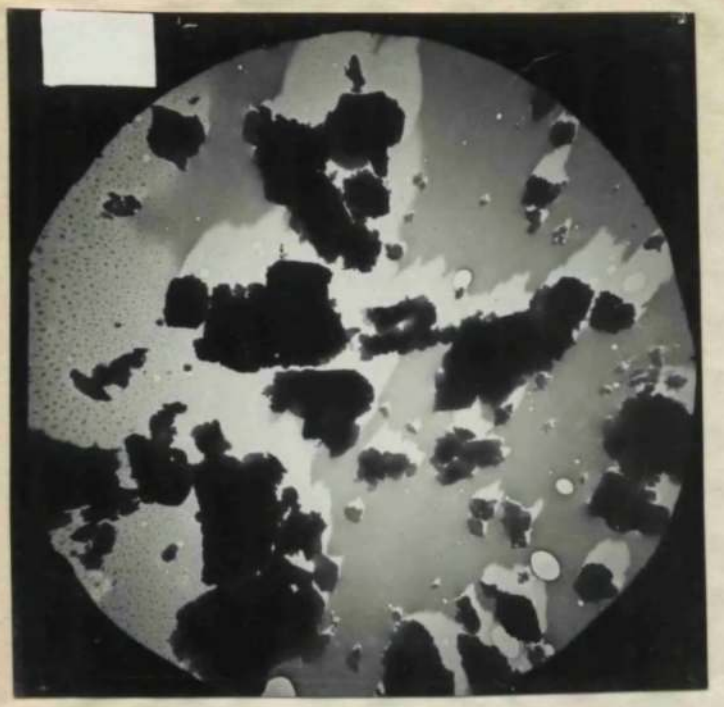


Plate 5
Airborne Coal Dust L.V.1.
(2600 X)

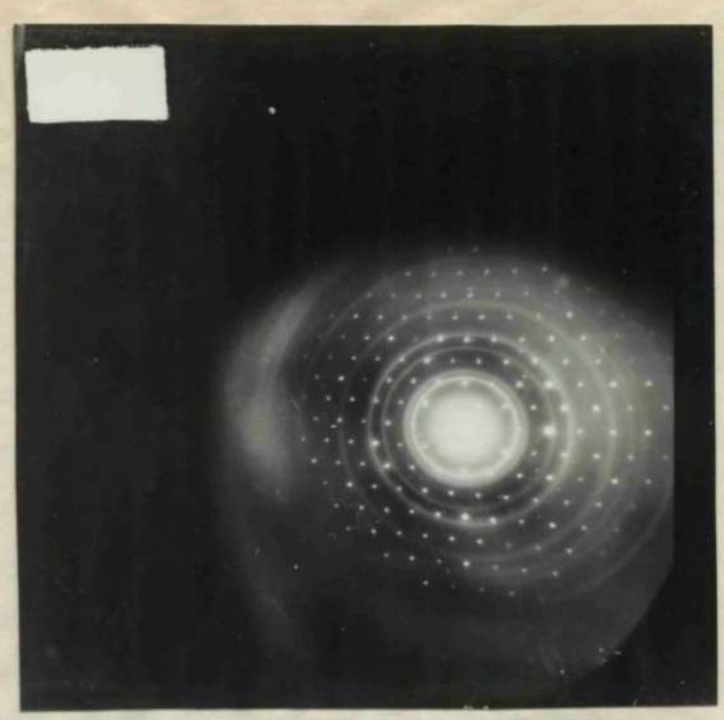


Plate 6
Electron Diffraction Pattern
C.1. Coal Dust

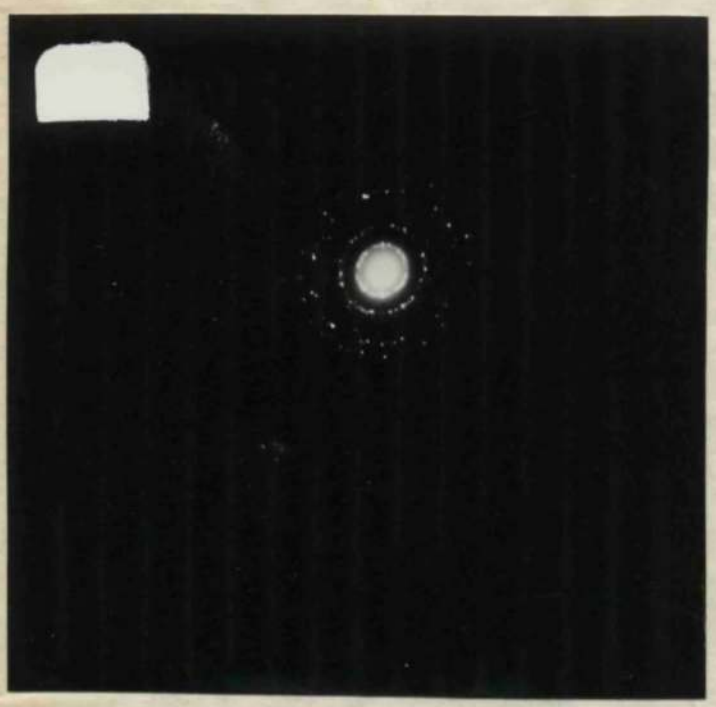


Plate 7
Electron Diffraction Pattern
1.K.1. Coal Dust

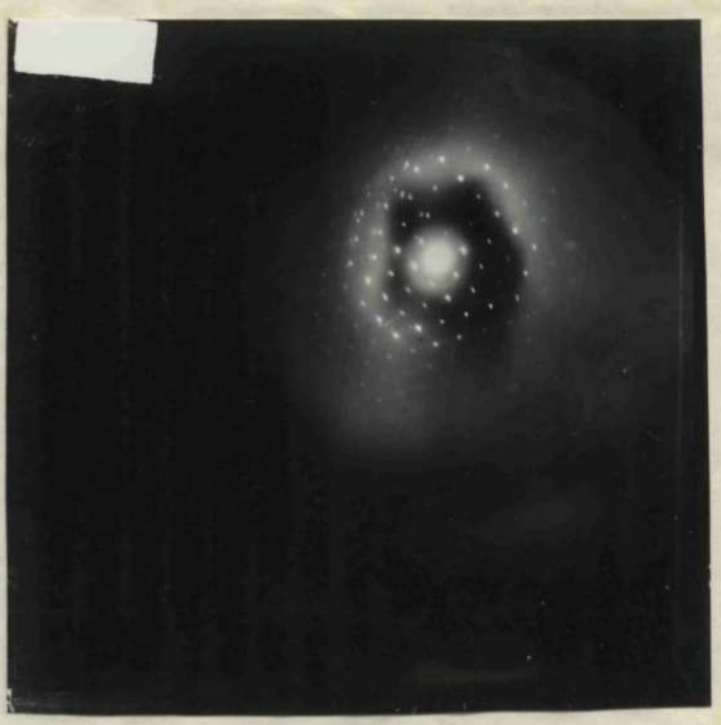


Plate 8
Electron Diffraction Pattern
L.V.1. Coal Dust

crystal will give rise to an orderly arrangement of spots, while a number of small crystals will result in a pattern composed of a number of concentric circles of light.

Electron diffraction patterns were obtained for most of the airborne colliery dusts collected. Apart from diffuse halos, three types of interference pattern were obtained, firstly patterns consisting of various concentric circles of light from areas composed of numbers of small crystals, secondly a cross-grating pattern consisting of diffraction spots arranged in hexagons from one type of crystalline particle and finally a cross-grating pattern composed or rings of spots, in which each ring of spots had a central diffraction spot, from another type of crystal. Examples of the type of interference pattern obtained are shown in Plates 6 to 8, but the cross-grating patterns obtained could not be definitely established as being due to any particular type of crystal, although the hexagonal type of cross-grating pattern mentioned above was very similar to the pattern obtained from mica crystals.

Apart from the difficulty of establishing the source of a given cross-grating pattern, the electron beam only penetrates the crystal structure to a very limited extent, thus a crystalline particle possessing an outer amorphous, or Beilby layer, could easily result in only a diffuse halo of light being obtained on diffraction. Apart from this factor an obvious statistical factor is involved as specimen areas no more than 7 microns in diameter may be examined at any one time and thus a large number of such areas must be examined before a reliable conclusion may be reached as to even the surface crystallinity of a given sample.

In view of these drawbacks no practical significance is at present given to these results.

SPECIFIC SURFACE ESTIMATION

General

Specific surface data for collected airborne dust samples were desired for two reasons, firstly to act as a rough check upon the results of microscopic size analysis, and secondly to estimate the total area available for reaction in a given weight of dust as this might well influence the velocity of any pathogenic reaction taking place within the lung. It is unlikely, of course, that the total available surface of the airborne dust will be the chief factor controlling the velocity of the pathogenic change taking place in the lung, particularly in the case of a heterogeneous dust such as coal mine dust, but the subject is nevertheless worthy of investigation.

The specific surface of a powder may be estimated using a number of different techniques, such as optical or electron microscopy, air permeability methods, low temperature gas adsorption, sedimentation techniques, light scattering methods and a variety of other methods which are mostly developments of the above techniques. The three methods of specific surface estimation employed in this work and the correlations found to exist between them are discussed in the following text.

Optical Microscopy

The particle size distribution of a dust may accurately be determined using an efficient optical microscope provided that the dust is substantially above 0.3μ in minimum particle size and provided that dispersion errors can be eliminated. The specific surface of the dust (7) may then be determined, if certain assumptions are made with regard to particle shape.

Specific surface, as customarily defined, is the surface per gram of material. Expressed in the form of an equation :

$$S = \frac{(\Sigma n s)}{\rho(\Sigma n v)} \qquad \text{----------} \quad (7)$$

where S = specific surface in cm^2/g.

ρ = true density of particles in $g./cm^3$

v = volume of a given particle in cm^3

s = surface area of a given particle in cm^2

or, assuming geometrical similarity between the particles and putting $v = \gamma' d^3$ and $s = \rho' d^2$ where γ' and ρ' are shape factors, we have

$$S = \frac{\frac{\rho'}{\gamma'}}{\rho \frac{(\Sigma nd^3)}{(\Sigma nd^2)}} \quad \text{---------- (8)}$$

Hence it follows that

$$d_3 = \frac{\Sigma nd^3}{\Sigma nd^2} \quad \text{---------- (9)}$$

is the average diameter from which the specific surface can be determined knowing the shape factor ρ'/γ'. If the diameter is restricted to 6v/s as in the cases of the diameter of a sphere, the side of a cube, or the harmonic mean of the sides of a rectangular parallellopiped, then maintaining geometric similarity.

$$S = \frac{6}{\rho\left\{\frac{\Sigma nd^3}{\Sigma nd^2}\right\}} \quad \text{or} \quad S = \frac{6}{\rho d_3} \quad \text{---- (10)}$$

The use of equation (10) in conjunction with particle size distribution data to obtain a specific surface value threfore involves two assumptions, namely that the particles display geometric similarity to each other and that they are approximately spherical in shape. As will be seen on examination of the electronmicrographs shown in Plates 1 to 6 neither of these assumptions ~~are~~ is justified with regard to airborne coal mine dusts. It is however difficult to estimate the shape factor ρ'/γ' and to allow for the lack of geometrical similarity between

particles, and equation (10) is generally resorted to when estimating the specific surface of a dust from size distribution data, although the result can be regarded as no more than a rough approximation.

It will be seen that using equation (10), it is necessary to know the true density of a dust in order to estimate its specific surface. The densities of the dust samples were therefore determined using the normal pycnometric method, modified slightly as it was found necessary to apply vacuum to the samples before the final weighing to remove occluded air bubbles in the containing liquid.

The tared density bottles containing known weights of dust samples were therefore half-filled with a containing liquid and slowly evacuated in a vacuum desiccator, being finally evacuated to a pressure of 10 mm. Hg. and left under vacuum for 24 hours. The vacuum was then released and the bottles topped-up before the final weighing.

Water was found to be unsatisfactory as a containing liquid owing to its high surface tension, which prevented the dust from being wetted, and led to splashing with loss of solid in the subsequent evacuation. Kerosene was found to wet the surface of the dust efficiently, but resulted in the slow dissolution of some of the dust constituents rendering it unsuitable for submission to any subsequent analytical process. 1% aqueous solutions of various salts were next examined for suitability as containing liquids and a 1% aqueous solution of "Teepol" (sodium salt of dodecyl benzene sulphonic acid) was found to be satisfactory although other acqueous salt solutions might well be equally effective.

The density bottles were thermostated in a water bath before performing the final weighing and the density of the containing liquid was taken to be that of water at the temperature of the bath after a small correction (+0.005 g./cc.) had been applied to allow for the dissolved "Teepol".

The values obtained for the apparent densities of various dust samples omitting and including the evacuation step are given in Table 7.

As is to be expected, the density figure obtained after evacuation had been employed is greater than the figure obtained where no evacuation step was included. It will be seen that the densities of the colliery dust samples were normally between 1.5 g./cc. and 2.0 g./cc., which seems reasonable since the specific gravity of pure coal is between 1.25 and 1.4, of shale 2.5, and of pyrites 5.

Table 7

DENSITIES OF DUST

Dust	Silica Dust		Coal Dust		
	M.S.C.	D.R.C.	C.1	P.1	C.4
Apparent density omitting evacuation step (g./cc.)	2.55	2.46	1.09	1.49	1.53
Apparent density including evacuation step (g./cc.)	2.65	2.66	1.75	1.75	1.90

Using the technique described above the density of each dust sample may be established to $\pm$ 2% using one gram of dust in 25 ml. of containing liquid, and the dust recovered after filtration and washing is unaltered and suitable for submission to subsequent analytical processes.

The microscopic method of estimating the specific surface of a dust is, of course, also subject to errors incurred in determining the size distribution. Thus both dispersion and sampling errors, as described in the section on optical microscopy, may have a considerable influence on the result. The effects of both dispersion and sampling errors are shown in Table 8, which gives the specific surface values calculated for four airborne dust samples from size distribution data, obtained by examinining slides prepared in three different ways under the optical microscope. The slides were obtained (A) by redispersing the collected dust by spraying, (B) by a thermal precipitator underground, but without any effort to ensure that the slide taken was representative of the

average condition of the dust cloud, and (C) by selection from a number of thermal precipitator slides taken underground so that the slide selected was representative of the mean concentration of the dust during collection.

Table 8

Effect of Dispersion and Sampling Errors on Specific Surface

(Values obtained using the optical Microscope)

Sample	Specific Surface ($cm^2/g.$)		
	Value obtained using slide as in (A)	Value obtained using slide as in (B)	Value obtained using slide as in (C)
C.2	3,470	7,000	5,200
C.3	3,300	4,700	5,360
C.4	3,100	5,550	5,360
3.K.4.	4,170	7,300	9,220

It is seen that the result is invariably lower using slides obtained as in (A) than the result obtained using slides of types (B) or (C) due to inability to completely redisperse the collected dust. However there is seen to be an approximate agreement as to order of magnitude between the result using slides obtained as in (C) above and the result using slides of type (A) and the ratio of the two results is also approximately constant. No such correlation exists between slides of types (A) and (B) and this is obviously not due to variation in the dispersion error but to the presence here of a large sampling error in addition to the dispersion error, no effort having been made with slides obtained as in (B) above to ensure that the slides were representative of the average condition of the dust cloud collected.

To obtain a reliable value for the specific surface of a dust from optical size distribution data it is therefore necessary to estimate the shape factor of the dust and to estimate or eliminate the dispersion and sampling errors involved in determining the size distribution data. These obstacles can be overcome in practice only at the expense of a great deal of labour.

Air Permeability Methods

The specific surface of a powder may be determined from known correlations by forming a packed bed of known porosity and depth from the powder and measuring the pressure developed across the bed for a given gas flow. The porosity of a packed bed is of course readily calculated, if the true density of the powder is known, from the dimensions and weight of the bed.

The particular adaptation of this technique employed in this work was the Lea and Nurse method, for which apparatus was readily available, and the specific surfaces of the dust samples employed were calculated using a development of the Carman equation (16) which corrects for "slip-flow" of gas around the sides of the compacted bed. This equation is shown below together with the particular values of the constants which applied in this case.

$$\frac{h_2}{h_1} \times \frac{CLK}{\varepsilon A g} = \frac{1}{S^2} \left\{ \frac{\varepsilon}{(1-\varepsilon)\rho} \right\}^2 + \frac{1}{S} \left\{ \frac{2\varepsilon \times \lambda}{(1-\varepsilon)\rho} \right\} \quad \text{---------- (11)}$$

where h_2 = difference in height on flowmeter (cm.)

h_1 = difference in height on manometer (cm.)

C = flowmeter constant (4.006×10^{-6} in this case)

L = bed depth (1 cm. in this case)

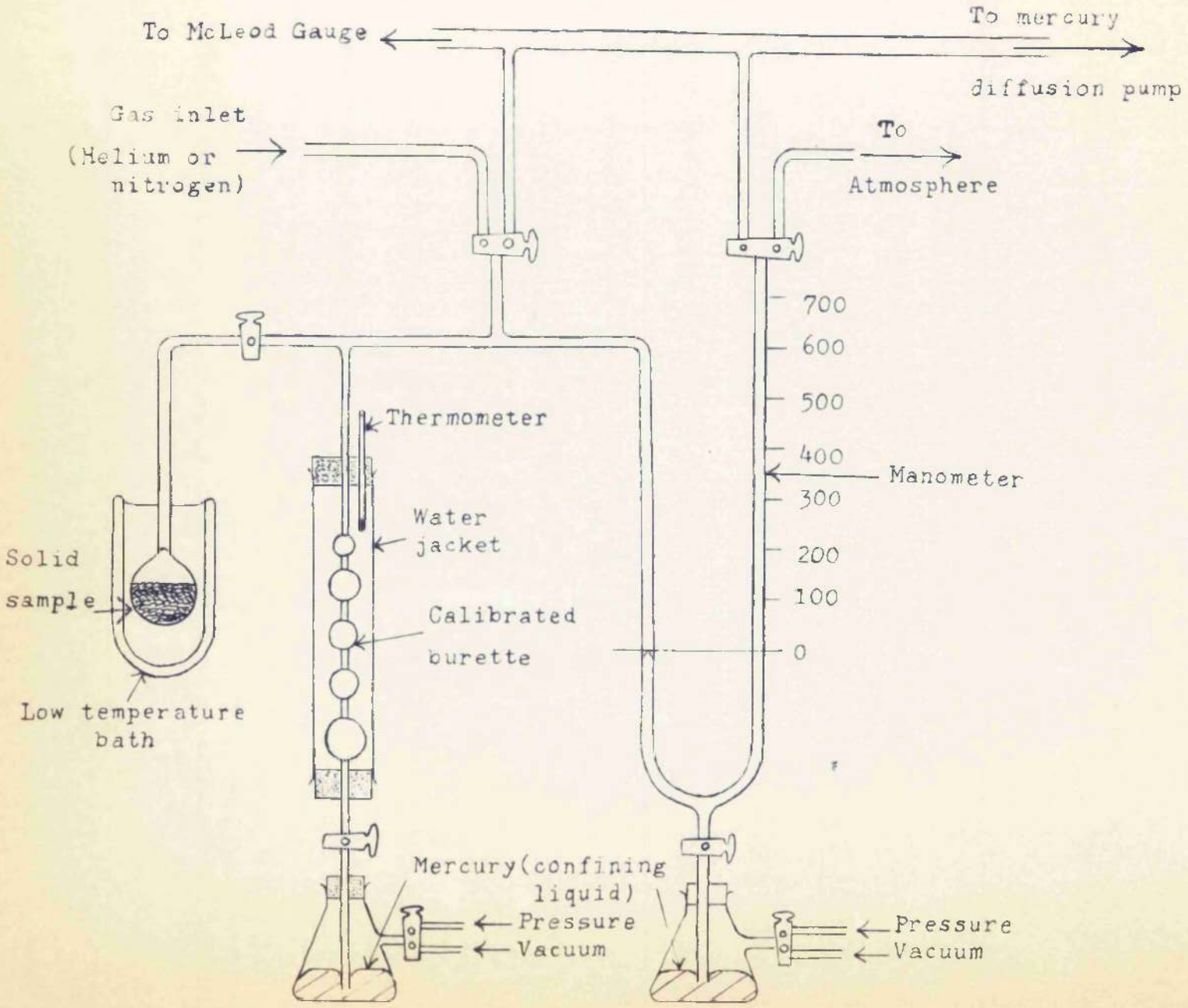
K = correction factor = 5

ε = porosity

A = cross-sectional area of bed (5.07 $cm.^2$ in this case)

Fig 10

Low Temperature Adsorption Apparatus



g = gravitational constant = 981 cm./sec.^{2}
S = Specific surface (cm.^{2}/g.)
p = true density of solid (g./cm.^{3})
x = correction factor = 0.874
λ = mean free path of gas molecules (9.6×10^{-6} cm. in this case)

It was found that a porosity of the order of 0.475 was required in order to obtain reproducible results and it can be seen from the dimensions of the apparatus employed that such a porosity requires 2.66 cc. or approximately 5 g. of dust. It was only possible therefore to obtain the specific surface of a few large dust samples using the available apparatus.

However using these quantities of dust it was possible to determine a specific surface value for a colliery dust sample which was reproducible to within ± 1.5% and it is probable that no appreciable deterioration in reproducibility would have resulted if the aparatus had been modified for use with a smaller dust cell. Insufficient time was however available for this to be done.

Low Temperature Gas Adsorption

The specific surface of a fine dust, such as airborne colliery dust, may be obtained from measurements of the physical adsorption of a gas, near its boiling point, upon the surface of the dust. Such measurements are employed to obtain an adsorption isotherm for the dust, from which it is normally possible to estimate the volume of gas necessary to form a monomolecular film around the sample and hence, knowing the area occupied by one gas molecule, it is possible to calculate the specific surface of the sample.

The apparatus employed in these investigations is shown diagramatically in Fig 10 and is seen to consist essentially of a sample bulb, calibrated gas burette, manometer, McLeod Gauge and high vacuum pumping system. The adsorbent, which was required to have a surface area of more than two

square metres, was evacuated in situ to 10^{-6} mm. Hg. at 110°C to remove water vapour and physically adsorbed gasses. The "dead space" above the adsorbent was then measured using pure helium. A volume of helium was admitted to the burette and measured in the usual manner. After the desired cold bath (liquid nitrogen at 77 - 78°K or liquid oxygen at 90°K) had been placed around the sample bulb, the stop-cock to the evacuated sample bulb was opened and the "dead space" was determined by again measuring the volume of helium in the burette. The adsorption of helium at this temperature is sufficiently low to be neglected. The system was then evacuated to 10^{-6} mm. Hg. and the "dead space" estimation was repeated to check any error. The system was then evacuated to 10^{-6} mm. Hg. once more in order to remove helium, and the stop-cock to the sample bulb was closed.

The adsorbate used in these experiments was nitrogen on account of its inertness towards the typical adsorbent, airborne colliery dust, and a suitable volume of this gas was now admitted to the burette and its volume was measured, the stop-cock to the evacuated sample was then opened and the volume of nitrogen remaining in the burette was measured, after time had been allowed for equilibration. The volume of gas adsorbed is then given by the equation

$$V_a = V_t - V_h \quad (1 + \alpha) - V_b \quad \text{- - - - - - - - - - (12)}$$

where V_a = volume of nitrogen adsorbed by sample (N.T.P.)

V_t = total volume of nitrogen which has been admitted to the system (N.T.P.)

V_h = volume of adsorbate rqquired to fill the "dead space" to the pressure, p, of the experiment.

α = correction factor required to take into account the gas imperfection of the adsorbate at the temperature of the cold bath.

V_b = volume of nitrogen remaining in buretie after adsorption (N.T.P)

Fig 11

Adsorption Isotherm for Nitrogen on D.R.C. Silica Dust

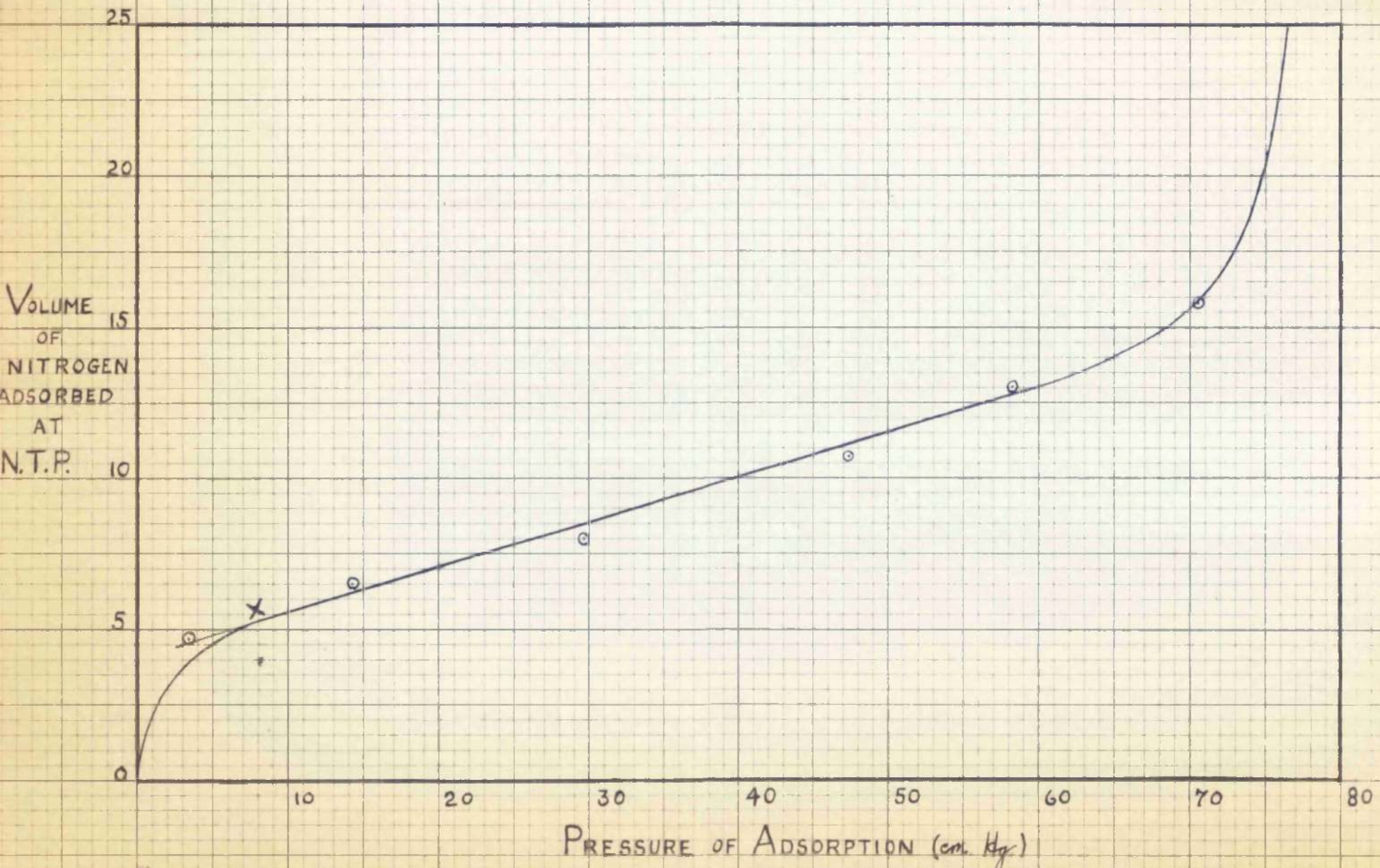
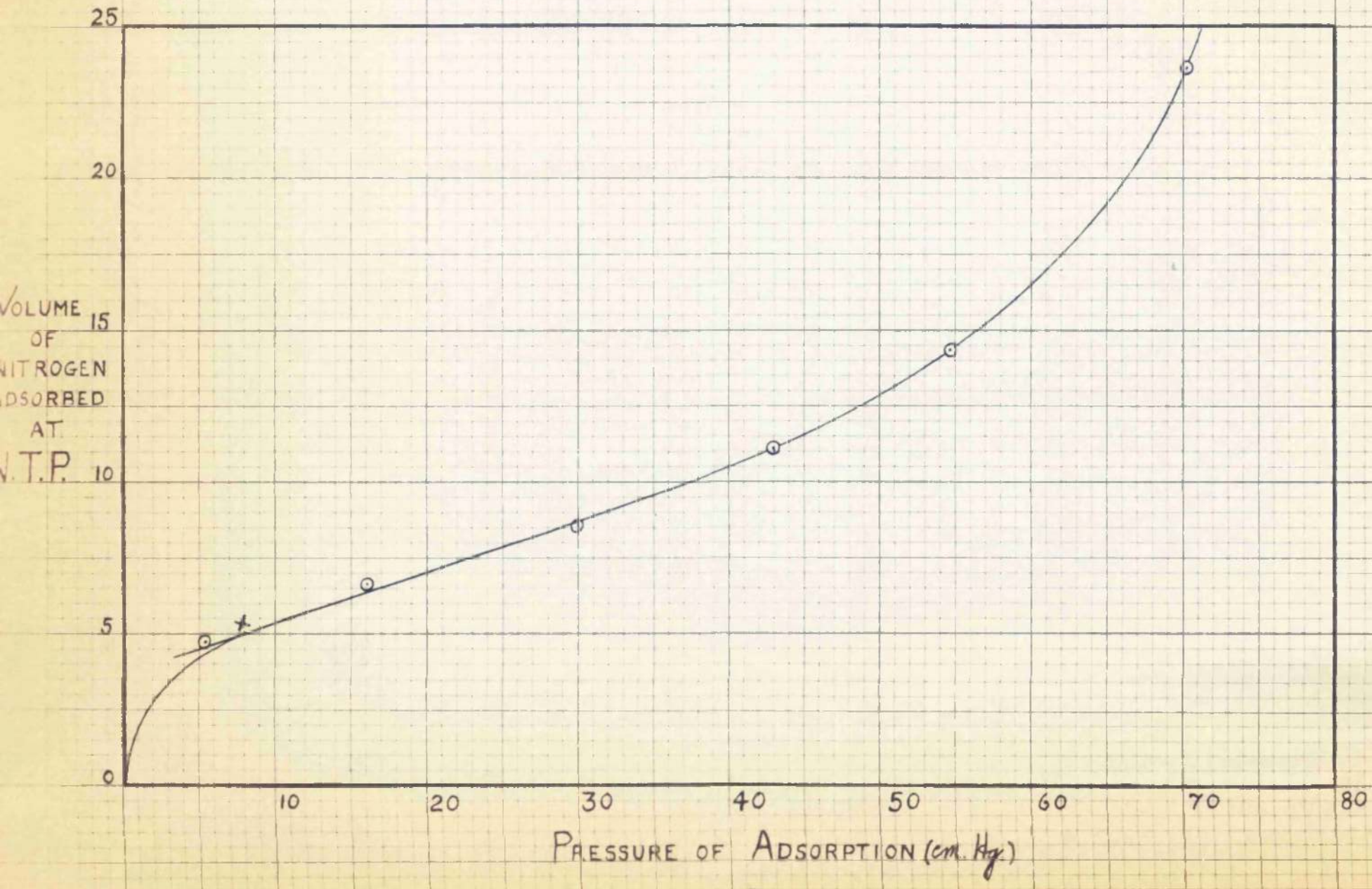


Fig 12

Adsorption Isotherm for Nitrogen on C.4 Coal Dust



By repeatedly adding more nitrogen to the system and noting the volumes adsorbed at the various pressure values an adsorption isotherm may be drawn for the material.

The use of such an isotherm in measuring the surface area of a sample obviously entails (a) selecting a point on the curve corresponding to the completion of a monolayer of adsorbed molecules and (b) assigning a value for the average area covered by each adsorbed molecule (17). The selection of the point corresponding to a monolayer is the crux of the entire problem and both an empirical and a theoretical method have been derived. In assigning a value to the average area occupied by an adsorbed molecule it has seemed reasonable to calculate the diameter of the adsorbed molecules from the densities of the liquefied or of the solidified adsorbate. If the physically adsorbed molecules are close packed on the surface one arrives at the following equation for the average area per molecule.

$$\text{area per molecule} = 4\ (0.866)\left[\frac{M}{\sqrt[4]{2\,N\rho}}\right]^{2/3} \quad -- \quad (13)$$

where M = molecular weight of gas

N = Avogadro's Number

ρ = density of solidified or liquefied gas

This equation is derived on the assumption that the molecules are hexagonally close-packed in the solidified and in the liquefied gas. For solid nitrogen, argon, carbon monoxide and a number of other gases such close-packing is known to exist, since these gases when solidified have face centred cubic packing. The values for liquid nitrogen are 17.0 Å^2 (90°K) and 16.2 Å^2 (77 - 78°K)

The type of adsorption isotherm obtained, using liquid nitrogen as coolant, for both commercial silica dust and airborne colliery dust is shown in Figs 11 and 12. It will be seen that both curves are sigmoidal in form and it is for this sort of curve that the relationships

governing physical adsorption of a gas upon a solid have been most firmly established.

On the basis of considerable empirical information the points X on the curves, corresponding to the start of the linear sections of the isotherms, have been considered to correspond approximately to completion of a monolayer of adsorbed gas for some time. More recently however Brunauer, Emmett and Teller (18) have developed a theory to explain these sigmoidal type adsorption isotherms which postulates the building up of multimolecular adsorption layers on the particle surfaces. They carried out a derivation for multimolecular layers that is similar to Langmuir's derivation for unimolecular layers and by means of a simplified summation obtained the following equation.

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{(c - 1)p}{v_m c\, p_o} \quad ----- (14)$$

where v_m = volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer.

p_o = liquefaction pressure of the adsorbate at the temperature of the experiment

c = constant which is dependent on the difference in the energy of adsorption between the first (E_1) and subsequent (E_2, E_3) ..... etc.) layers and is approximately given by $c^{-(E_1 - E_2)/RT}$

The application of equation (14) is to find V_m. A plot of $\frac{p}{v(p_o - p)}$ versus $\frac{p}{p_o}$ yields a straight line from the gradient and intercept of which both v_m and c can be calculated. The method has two advantages over the graphical selection of point X, namely that it is not susceptible to the uncertainty that is involved in selecting point X graphically and that fewer experimental readings are required.

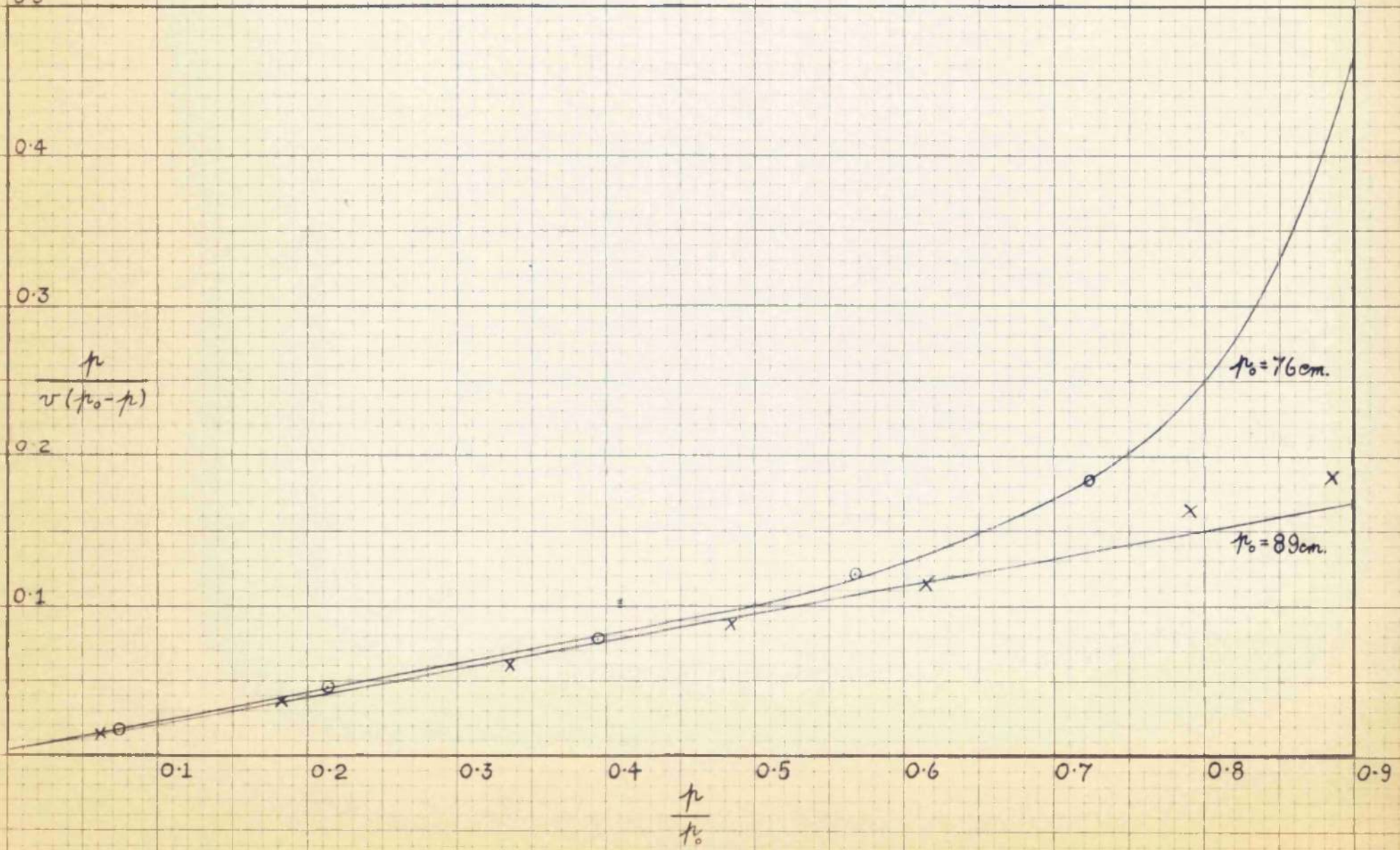
Both liquid nitrogen and liquid oxygen were used as coolants in these investigations, the liquefaction pressure of nitrogen at the temperature of liquid oxygen (90.2°K) for use in equation (14) being calculated from the formula developed by Dodge and Davis (19) as approximately 273 cm. Hg. The disadvantage of using liquid nitrogen as a coolant is that the bath slowly condenses oxygen from the surrounding atmosphere, and hence slowly rises in temperature throughout the run. The liquefaction pressure of the nitrogen adsorbate, p_o, will therefore not be atmospheric pressure but some indeterminately higher figure depending on the amount of oxygen dissolved in the bath. This effect or rising bath-temperature is shown in Figs 12 and 13 as the isotherms do not become asymptotic to the y-axis until well above atmospheric pressure. Using liquid oxygen as coolant this effect is eliminated, but since 1.5 atmospheres is about the maximum safe pressure which may be used in normal glass apparatus, the adsorption isotherms obtainable are consequently limited to fairly low relative pressures in this case.

In order to investigate which of these coolants would be most effective in estimating specific surfaces nitrogen adsorption runs were performed in duplicate on two dust samples (commercial "D.R.C." silica dust and airborne colliery dust sample C.4.) using both liquid nitrogen and liquid oxygen as coolants, on approximately 4 g. of dust, about the most likely to be obtained in underground collections, and plotting the adsorption isotherm up to pressures of about 1.5 atmospheres. The results given in Table 9 show the effect of rising bath temperature, when using liquid nitrogen coolant by the slightly lower average result obtained in this case. However the reproducibility using liquid nitrogen as coolant is much higher than that obtained using liquid oxygen and this is undoubtedly due to the uncertainty of determining the monolayer adsorption volume, v_m, owing to the low limit placed upon the relative pressure obtainable using

Fig 13

Application of B.E.T. Equation to C.4. Coal Dust

Effect of alteration in value taken for p_0



the latter coolant. Agreement between the values for specific surface obtained using liquid oxygen as coolant was not materially improved by applying the method of least mean squares to obtain the best possible solution of equation (14) from the experimental results.

Table 9

Comparison of Coolants employed in B.E.T.Method

Coolant employed		Liquid Nitrogen		Liquid Oxygen	
Dust employed		D.R.C. (Silica)	C.4 (Coal)	D.R.C. (Silica)	C.4. (Coal)
Specific Surface ($cm^2/g.$)	Run 1	53,200	54,800	51,600	81,000
	Run 2	51,700	51,900	61,200	35,600
	Average	52,450	53,350	56,400	58,300

In order to obtained reasonable accuracy conveniently it is therefore better to employ liquid nitrogen as coolant although the slowly rising bath temperature will lead to the production of an error if equation (14) is applied to the results and the value of p_o taken to be atmospheric pressure as shown in Fig 13. This source of error can be largely reduced however and a reasonable approximation to the value of v_m may be obtained if any of the following expedients are adopted, namely (a) direct plotting of the isotherm to give v_m as previously described, or (b) using equation (14) and confining the values employed in its solution to relative pressures of less than 0.5, or (c) graphical interpolation for a value of p_o such that equation (14) becomes linear and then solving the equation using all the results available. As shown in Table 10 little variation exists between the values of specific surface obtained from given experimental results using any of the above methods of calculation.

Table 10

Variation of B.E.T. Result with Method of Calculation

Specific Surface Values ($cm^2/g.$)

Dust employed	Method of Calculation		
	(a) above	(b) above	(c) above
D.R.C. (Silica)	54,600	53,200	56,400
C.4. (Coal)	52,550	54,800	56,200

When liquid nitrogen is employed as coolant a reproducibility of better than $\pm$ 10% is obtainable in the specific surface values from low temperature adsorption determinations carried out on 4 g. of dusts of the type collected in these investigations. The experimental error is however proportionately increased as the total surface available for adsorption is decreased and thus approximately 1 g. of typical airborne colliery dust is required in order to give a reproducibility of $\pm$ 50%.

Correlation between Methods

The values obtained for the specific surface of five different dusts determined by four different methods, namely (a) low temperature nitrogen adsorption, (b) the Lea and Nurse air permeability method, (c) microscopic analysis of a thermal precipitator slide taken from the original dust cloud and representative of its mean concentration and (d) microscopic analysis of the collected dust after redispersion, are given in Table 11. It will be seen that the values obtained for the specific surface of any of the samples decrease in the order (a) (b) (c) (d) and this is in accordance with the results of other workers (20) (21)

Table 11

Comparison of Methods for Specific Surface Determination

Dust Sample	Specific Surface ($cm^2/g.$)			
	(a) Low Temp Nitrogen Adsorption	(b) Lea & Nurse	Microscopic Analysis (c) T.P. Slide	Microscopic Analysis (d) Redispersed dust
M.S.C. Silica	51,500	15,100	-	5,970
D.R.C. Silica	52,450	16,000	-	6,780
C. 1 Coal	26,100	12,560	-	4,320
P. 1 Coal	27,700	12,480	-	4,550
C. 4 Coal	53,350	12,280	5,390	3,110

The increase in the specific surface value obtained using method (c) over that obtained using method (d) above is to be expected owing to the absence of any dispersion error when method (c) above is employed. Similarly the increase in specific surface value obtained using an air permeability method over that obtained using microscopic analysis may also be readily explained by the fact that the particles are no longer treated as equivalent spheres using this method. This assumption, which is in fact unjustified with regard to airborne colliery dust, was made when calculating specific surfaces from microscopic distribution data and better correlation between the air permeability results and the microscopic results might well have been achieved if a reliable shape factor for the dust had been obtainable.

The increase in the specific surface values of dusts as calculated from low temperature nitrogen adsorption isotherms over those calculated from air permeability methods or microscopic analysis requires a more

lengthy explanation. It is assumed in air-permeability methods that the bed of powder behaves as a bundle of capillaries. In consequence, only the surface of the continuous paths through the material will contribute to the measured specific surface area. This area is not the same as that measured by adsorbing a gas on the surface of a powder where all the surface accessible to gas molecules of the type used will contribute and there will therefore be a general trend for results obtained from adsorption data to be larger than those obtained by a permeability method. This difference may be accentuated if the powder has an appreciable internal surface due to cracks, internal pores and other irregularities and, in addition the permeability methods may not measure the full external surface of the powder because of the formation of blind pores during compaction.

Thus when a very much larger specific surface figure is obtained using a low temperature adsorption method than the specific surface figure obtained by an air permeability method on the same powder, particularly where the powder is coarse and the ratio between the results is greater than 10, a considerable internal surface is indicated in the powder. Where the ratio of the two results is in the range 2 to 5, however, as was found to be the case in these experiments, no definite conclusion on the presence or absence of internal surface can be drawn, although it seems likely that at least a small amount of some form of internal surface may have been present.

It is however obvious that, while agreement within any one method is fair, agreement between different methods is poor, each method giving a completely different range of answers.

Conclusions

The method to be employed in measuring the specific surface of an airborne colliery dust will depend on the particular aspect of the properties of the dust under consideration. If ability to penetrate to the terminal air sacs of the lung is the question under

consideration, then the external surface of the particles is the primary factor concerned and microscopic analysis corrected by the use of a suitable shape factor or an air permeability method, preferably adapted for use with small amounts of dust, may be employed. The latter method has the advantage of being much the more rapid of the two methods.

If the factor under consideration is the total surface available to take part in a heterogeneous chemical reaction, then it is probable that a low temperature adsorption method should be adopted although this technique is rather lengthy and requires relatively large amounts of dust.

In investigations of this type however, it is probably best merely to check the results of optical microscopy by means of a suitably adapted air permeability method, which can be executed rapidly using small quantities of dust.

EXAMINATION OF COLLIERY DUSTS BY X-RAY DIFFRACTION

Introduction

Since the wavelength of X-rays, commonly 0.1 to 1 Å, is of the same order as the interatomic distances in typical crystal structures, crystals act in the manner of diffraction gratings when irradiated by X-rays and give rise to interference patterns. The distances between the various interference bands is dependent upon the interatomic distances in the crystal, and the intensity of each reflection is dependent upon the atomic number of the atom causing the reflection, thus a pure crystal generally yields a characteristic diffraction pattern by which it may be identified. Amorphous material on the other hand does not give rise to a regular diffraction pattern, since the interatomic distances in such material are naturally not consistent.

It was therefore decided to investigate the crystal structure of some of the airborne colliery dust samples by means of X-ray powder diagrams and thus obtain some preliminary idea of the degree of crystallinity present. It was intended to use the diffraction patterns to estimate the quartz contents of the dusts by comparison with known standards.

Procedure and Results

Powder photographs were taken in a 5.73 cm. diameter unevacuated diffraction camera with filtered copper radiation. The sample to be irradiated was loaded directly into lithium borate glass tubes of 0.5 mm. outside diameter and 0.3 mm. bore. In general, dusts were not sieved but were used exactly as they came from the collector so that the full particle size range was present in the specimen.

In all cases continuous diffraction rings were obtained and the "d" spacings of the rings were measured by Ångstrom scale since the absence of high angle reflections prevented more accurate measuring techniques being adopted. The patterns obtained for the various colliery dust samples were then compared with the lines obtained from

standard samples of quartz, kaolinite and illite, kaolinite being taken as a typical example of the kaolin group of minerals, and illite being taken as representative of the micaceous group of minerals. The results obtained by examination of x-ray powder diagrams for a series of pilot samples together with the results of chemical analysis for free and total silica are given in Table 12 below.

Table 12

Interpretation of X-ray Powder Diagrams

Sample	% Free Silica	% Total Silica	X-ray Powder Diagram Result
3.K.1	4.4	15.4	Faint silica line Faint silicate lines
C. 1	5.3	12.0	Weak silica lines
3.K.2	4.0	14.5	Faint diffuse silica lines (small particles)
1.K.1	3.2	21.2	Weak silica lines
L.V.1	5.4	20.8	Weak silica lines
P. 1	4.4	9.0	Weak silica. Apparently present in large particles
E.F. 1	1.0	21.3	Faint silica lines. Strong silicate lines
M. 1	12.7	30.7	Weak silica lines. Weak silicate lines
V. 1	2.7	7.6	Faint silica lines. Weak silicate lines
L. 1	4.7	16.0	Weak silica lines. Weak silicate lines

It will be seen that no more than a very rough idea of the composition of the colliery dust was obtained from the x-ray powder diagrams, although some form of agreement is obviously present. Thus in sample E.F.1. the kaolinite lines are stronger than the quartz lines, in contrast to the remaining samples, and this result is confirmed by the results of chemical analysis.

Attempts were made with later samples to simplify the diffraction patterns by ashing the samples at 750°C prior to examination to remove the coal fraction of the dust. The ashing process was found, however, to result in the destruction of several of the minerals in the dust, including kaolinite, and little improvement in the clarity of the diffraction pattern resulted probably owing to the presence of considerable amorphous material in the ashed sample.

Conclusions

The simple technique used does not give worthwhile results even though as little as 3% of silica can be detected.

Interpretation of the diffraction patterns is rendered difficult by the presence of considerable amorphous material which is not readily removed, and, in addition, since clay minerals are generally of layer form, it would be necessary, if an analysis of those were required, to modify the camera to record lower diffraction angles. For example, 9 Å is the largest "d" spacing which could be measured with the instrument employed, while 10 Å is the strongest line for illite. The camera would also require to be evacuated if a quantitative estimation of quartz content was required.

The problem of estimating the quartz contents of small particle size dusts by means of x-ray diffraction techniques has been largely overcome by Dr. Nagelschmidt of the Safety in Mines Research Establishment, Sheffield, who overcomes the problem of the existence of an amorphous layer around small silica particles (22) by determining a "mean quartz rating" for each sample. He has employed two methods

in his investigations. The first method employes cobalt K radiation and adopts a microdensitameter technique (23) using magnesium oxide as internal standard, this method is capable of an accuracy of ± 10% for samples containing more than 30% of quartz. The second method, which is a development of the first, is capable of an accurary of, at best, ± 4% (24) and uses a Geiger-Müller counter unit (25) specially built to employ an external standard.

It is therefore evident that it would be necessary to employ a counter technique similar to that employed by Nagelschmidt to obtain worthwhile accuracy in work of this kind and equipment of this highly developed type was not available for use in this investigation.

ESTIMATION OF THE FREE SILICA CONTENT OF DUSTS

Introduction

The ability to determine the free silica content of airborne dusts is of the utmost importance in estimating the health hazard they create. Several methods both chemical and physical have been developed for this purpose, the most popular of the physical methods being differential thermal analysis (26) and x-ray diffraction, while the sulphuric acid method of Shaw and Skinner (27) and the phosphoric acid method of Trostel and Wynne (28) have become generally accepted as suitable chemical methods. None of these methods, however, is capable of a high degree of accuracy.

Nagelschmidt has shown (24) in a series of inter-laboratory tests carried out on standard samples that a semi-micro modification of the Shaw-Skinner technique gives the more accurate results of the two chemical methods, while x-ray diffraction methods are capable of considerably greater accuracy than differential thermal analysis. Both the Shaw-Skinner technique and x-ray diffraction are capable, at best, of an accuracy of $\pm$ 4%.

Accordingly the semi-micro modification of the Shaw-Skinner method, described fully in Appendix A, was adopted for the estimation of the free silica contents of the airborne colliery dusts collected in this investigation.

Shaw-Skinner Method

The Shaw-Skinner method for the determination of free silica depends basically upon the dissolution of the silicate portion of the dust in hot concentrated sulphuric acid without attack upon the quartz content. As many silicates under these conditions release their silica in an amorphous form, insoluble in hot acid, this silica is removed by a dilute alkali extraction. After a series of such extractions a residue A is obtained. This residue is then treated with 40% hydrofluoric acid and

a non-siliceous residue B is obtained. This residue is taken to be alumina, and this amount, multiplied by 2.01, gives an estimate of the undecomposed silicates of the sample estimated as felspar. The free silica content of the sample may then be calculated from the formula below, in which the factor 108.6 has been incorporated to allow for the solubility of quartz dust of respirable size in hot acid and dilute alkali.

$$\% \text{ Free-Silica Content} = \frac{\{A - (B \times 2.01)\} \times 108.6}{\text{Weight of Sample}} \quad - - - - - - (15)$$

After each treatment in this method, the dust has to be separated from the supernatant liquid by centrifuging, and since untreated airborne colliery dust was not wetted by the various reagents, accurate results could not be obtained. This difficulty was, however, overcome by first ashing the colliery dust at 750°C for one hour in a muffle furnace before submitting it to analysis by the Shaw-Skinner technique. This modification also, naturally, resulted in an increase in the accuracy with which the silica content of the colliery dust was determined.

The samples of airborne dust obtained from the various pits arrived in the Soxhlet thimbles in which they had been collected. Each sample was then transferred to a tared Petri dish and dried under vacuum at 60°C for four hours. The dry dusts were all found to be hydroscopic to some extent and all increased in weight on the balance pan to the extent of up to approximately 0.5% of their total weight. While some error inevitably resulted from this source this error was very small in comparison with the error due to the inaccuracy of the analytical method employed, and the error due to moisture absorption was in any case rendered substantially constant in all the following analytical procedures by weighing the dust samples only after they had reached equilibrium with the air in the balance case, which was dried by silica gel, so that the moisture contents of the nominally dry dusts were, therefore, fairly constant.

When these precautions had been taken and the dust had been ashed before submission to the process of analysis it was found that a reproducibility of the order of ± 0.5% was obtained in the free silica content of the uncombusted colliery dust. Since the accuracy of the Shaw-Skinner method is approximately ± 4%, however, an accuracy of ± 0.5% will probably only in fact be obtained where the ash content of the colliery dust is less than 12.5%. The results of these analyses on colliery dusts, which were performed in duplicate, are given in the final section of this thesis.

In order to test the operator's accuracy and the accuracy of the method a number of standard samples, provided by Dr. Nagelschmidt for his inter-laboratory tests (24) were analysed using the semi-micro modification of the Shaw-Skinner technique and ashing the samples before submitting them to analysis in analogy with the procedure adopted when the method is applied to airborne coal mine dusts. The compositions of the standard dust samples employed and the results of their duplicate analyses are given in Table 13 below.

Table 13

Accuracy of Shaw-Skinner Semi-Micro Method
(Samples supplied by Dr. Nagelschmidt)

Sample	Known Composition			Analysis
	% Quartz	% Kaolinite	% Muscovite	% Free Sili
X1072	100	0	0	100.0
X 1876	0	100	0	1.2
X 2043	66.7	33.3	0	66.0
X 2431	0	0	100	0.5
X 2478	0	28.5	71.5	0.5
X 2479	14.0	24.6	61.4	17.0
X 2480	48.4	14.8	36.8	49.0
Maximum Error (%)			3.0	
Standard Deviation			1.3	

The method appears to have a slightly greater accuracy than that estimated by Nagelschmidt and seems capable of giving reliable information on the free silica contents of airborne colliery dusts. The fact that a result of 100.0% was obtained for sample X1072 is, of course, a coincidence, although this result appears to justify the value taken for the correction factor in equation (15).

Although the method is reliable and yields reasonably accurate results it is laborious and lengthy, requiring 18 to 20 man-hours for a duplicate determination. This factor is a severe handicap in work of this kind where a large number of results are required before any conclusions as to the dependence of health hazard upon dust composition may be drawn.

For this reason it was considered important to develop more rapid and, if possible, more accurate methods of free silica determination.

Infra-Red Spectra of Silica and Silicate Minerals

It was appreciated that the time required for the analytical process would be greatly reduced if the gravimetric method could be replaced by an optical method in which no complicated treatment of the dust was required. An attempt was therefore made to develop a method of free silica estimation using infra-red spectroscopy.

The atoms of a solid do not remain at rest but are continually in vibration at frequencies of the order of 10^{13} to 10^{14} cycles per second, which is of the same order of magnitude as the frequencies of infra-red radiation. These intra-molecular vibrations occur at certain frequencies depending on the grouping (e.g. C-H, C-O, C=O) and if substances are irradiated by a succession of monochromatic bands of infra-red radiation, these frequencies may be absorbed. It is possible, therefore, by plotting the percentage of radiation absorbed by a substance against the incident wavelength to state that a molecule contains certain groupings e.g. C=O and this function is carried out by

the infra-red spectrophotometer. The use of infra-red spectroscopy as an analytical tool has been developed, with a great degree of success, ih the field of organic chemistry, but its use in inorganic applications has only begun to be exploited over recent years.

In order to determine whether the infra-red spectrum of quartz contained absorption bands which are not shown by other minerals commonly to be found in colliery dust, the data obtained by Prentice (29), a previous worker in this field, and by other workers whose results are reported in the literature (30) (31) (32) (33) were referred to. This condition must be satisfied before a reasonably accurate estimate of quartz content may readily be made using infra-red spectroscopy.

The positions of the main absorption bands for minerals commonly found in colliery dusts are given in Table 14. Calcium carbonate has been included in the list as limestone and water are frequently used on the floors of headings in coal mines to reduce the explosion risk presented by accumulations of coal dust. It is therefore possible that airborne colliery dust could become contaminated with quantities of calcium carbonate entrained from the floor of the roadway by the ventilating air current. The data for cyclo hexane and for aluminium stearate which were later used to prepare dispersion mixtures are also given.

Table 14

Main Absorption Bands in Infra-Red Spectra of Minerals

Key s = strong, m = medium, w = weak

Substance	Wavelengths of Absorptions (μ)
Quartz	5.95 (w), 6.30 (w), 7.70 to 11.70 (s) 12.50 (m) and 12.85 (m)
Cristobalite, Tridymite and Fused Silica	5.95 (w), 6.30 (w), 7.70 to 11.70 (s) and 12.50 (m
Kaolinite	2.73 (m), 6.05 (w), 7.55 (w), 8.93 to 10.95 (s) 12.50 (m), 12.65 (m), 13.30 (w) and 14.51 (m)
Mica	9.30 to 10.80 (s) and 13.30 (m)
Muscovite	2.78 (m), 9.35 to 11.0 (s), 12.1 (w), 12.5 (w), 13.35 (m), and 14.8 (w)
Olivine	6.10 (w), 9.85 to 11.90 (s) and 13.10 (w)
Willemite	8.25 (w), 8.60 (w), 9.00 (w), 9.15 (w), 9.50 (w) and 10.00 to 11.55 (s)
Vitrain or Anthraxylon	3.0 (m), 3.30 (w), 3.42 (s), 5.22 (w), 5.87 (s) 6.19 (s), 6.90 (s), 7.25 (w), 8.0 (m), 9.67 (w) 11.64 (m), 12.26 (m) and 13.29 (m)
Calcium Carbonate	6.50 (w), 6.80 (s), 6.95 (m), 7.40 (m) and 8.70 to 10.05 (w)
cyclo Hexane	2.51 (w), 2.87 (w), 2.97 (w), 3.14 (w), 3.44 (s) 3.72 (s), 3.79 (s), 4.25 (w), 4.40 (w), 4.60 (w) 4.68 (w), 4.83 (w), 500 (w), 5.32 (w), 5.44 (w) 6.88 (s), 7.4 (m), 7.95 (s), 8.64 (w), 9.65 (m) 11.05 (s) and 11.6 (s)
Aluminium Stearate	6.35 (m), 6.85 (m) and 10.25 (w)

It is seen from Table 14 that, while quartz has absorption maxima at 12.50 μ and 12.85 μ, silicates with the exceptions of kaolinite and muscovite have no absorption maxima at these wavelengths

With the methods employed in this work however, it was impossible to detect the weak absorption bands shown by muscovite at 12.1 μ and 12.5 μ, while the absorption maximum shown by kaolinite at 12.5 μ was very much weaker than that shown by quartz at the same wavelength. It should be possible, therefore, to determine quartz in the presence of silicates including kaolinite and muscovite using the absorption maximum shown by quartz at a wavelength of 12.50 μ.

A study of the spectra obtained for the various forms of free silica shows that all forms (quartz, cristobalite, tridymite and fused silica) have an absorption maximum at 12.50 μ, but that only quartz has an absorption maximum at 12.85 μ. From this it may be concluded that it should be possible to estimate quartz in the presence of other forms of free silica, and this has in fact been achieved (34) using a pelleting technique. No such discrimination between quartz and other forms of free silica was however attempted in this investigation.

Similarly calcium carbonate, cyclo hexane and aluminium stearate give absorption spectra with no absorption maxima, at wavelengths of 12.5 μ or 12.85 μ, and these substances may therefore be present in any sample under examination for quartz content. Vitrain, a common coal constituent, does however show an absorption maximum in the region of 12.50 μ wavelength, but coal constituents may readily be removed from airborne colliery dust by ashing prior to spectroscopic examination.

Dispersion Method

In order to carry out a quantative estimation upon a solid by means of infra-red spectroscopic examination, where a dispersion technique is selected for the purpose of mounting the solid in the spectrsocope beam, the following conditions must be satisfied. Firstly, the particle size of the material under test must be less than 1 μ in order to minimize refraction of the incident infra-red light. Secondly, the material under test must be uniformly dispersed in the dispersion medium and, finally, a cell of uniform thickness must be employed.

Prentice did considerable work in adapting dispersion methods to the specific problem of free silica estimation and finally adopted a development of the technique employed by Dolinsky (35) who suspended various solids in 1% solutions of aluminium stearate in carbon tetrachloride or carbon disulphide for infra-red spectroscopic examination. It was decided to repeat the later stages of the work performed by Prentice before proceeding further with the investigation.

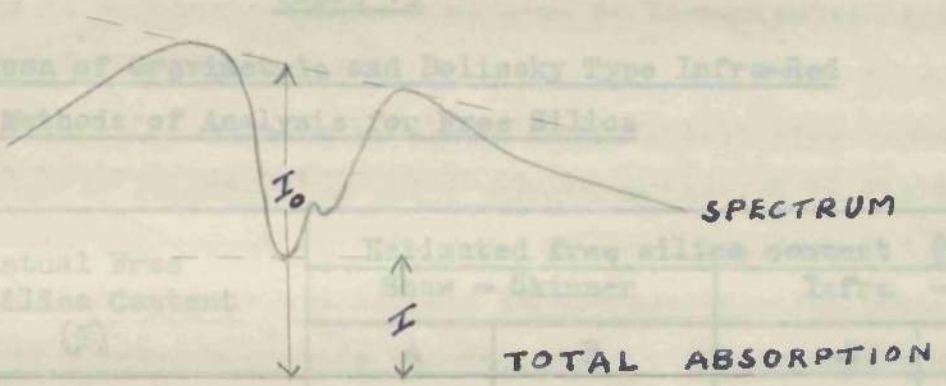
The standard samples, supplied by Dr. Nagelschmidt, were again employed in testing this method of free silica estimation. In analogy with the treatment which would be necessary for airborne colliery dusts, approximately 2 g. of each standard sample was first heated in a muffle furance at 750°C for one hour and the ash content estimated. The ash from this procedure was then ground for twenty hours in a mechanical agate mortar in order to reduce its particle size to less than 1-μ.

The material under test (1 g.), aluminium stearate (1 g.) and cyclo hexane (25 ml.) were them placed in a 250 ml. "Quickfit" flask and heated to boiling, with constant shaking. The flask was allowed to cool and glass beads (25 ml.) were added. The flask wasthen shaken for one hour on a "Microid" flask shaker, when the material was considered ready for analysis.

The infra-red spectrophotometer used in this work has been described by Brownlie (36) and uses a Schwarz thermopile in the receiving system. This spectroscope was used as a single beam instrument throughout these investigations on account of its diminished sensitivity when employed as a double beam instrument.

This spectrophotometer was found to be insufficiently stable to enable calibration curves to be employed successfully and therefore the base line method was employed in estimating the amount of absorption taking place at a wavelength of 12.5-μ, which was chosen as the characteristic absorption maximum for free silica, for reasons already stated.

In order to minimize the effect of variations in the sensitivity of the spectroscope all the spectrographs necessary for a series of duplicate estimations were obtained on the same day and fairly frequent spectrographs of the quartz standard (X1072) were obtained throughout the period of operation of the instrument. Using the base-line method (37) the concentration of a given material present is proportional to $\log_{10} \frac{I_o}{I}$ where the symbols have the significance indicated in the following sketch and the quantities are measured at an absorption maximum characteristic of the material concerned.



As had been noted by Prentice the accuracy of the method fell off rapidly, where the samples contained less than 50% of free silica, Thus, for samples containing less than 50% of free silica, 0.5 g. of sample and 0.5 g. of pure quartz were taken, instead of 1.0 g. of sample, when making the suspension.

A rock salt cell adapted for use with uniform thicknesses of viscous liquids was developed by Prentice for use with the type of mull obtained as above, and this cell, which is described below, was used in these investigations.

Two lead strips, measuring 1 in. by 0.1 in. and 0.005 in. thick, are placed lengthwise at opposite ends of a 1 inch square polished rock salt plate. A suitable quantity of the mull prepared for

examination is placed in the middle of this plate and a second similar rock salt plate is brought into position on top, care being taken to exclude all air bubbles from the cell.

The results obtained for the free silica contents of the standard samples, both by the method described above and by the Shaw-Skinner semi-micro method are given in Table 15. Since this work was originally performed by Prentice, this worker's results are quoted in columns A of Table 15, while the results obtained by the writer are given in columns B.

Table 15

Comparison of Gravimetric and Dolinsky Type Infra-Red Methods of Analysis for Free Silica

Sample	Actual Free Silica Content (%)	Estimated free silica content (%)			
		Shaw - Skinner		Infra - Red	
		A	B	A	B
X 1876	0.0	9.0	1.2	0.0	3.0
X 2431	0.0	4.2	0.5	0.0	7.3
X 2478	0.0	0.7	0.5	0.0	0.0
X 2479	14.0	16.4	17.0	15.0	19.9
X 2480	48.4	47.0	49.0	50.0	54.7
X 2043	66.7	65.5	66.0	68.0	61.1
X 1072	100.0	88.2	100.0	100.0	100.0
Maximum Error (%)		11.8	3.0	1.6	7.3

It will be seen that while Prentice found the infra-red method described above superior in accuracy to the Shaw-Skinner method, the writer found it rather less accurate, although it was undoubtedly considerably more rapid. This disagreement, however, could easily

have been caused by the varying skills of the operators at each of the two methods employed.

Pelleting Method

While the method of infra-red analysis for free silica developed by Prentice appears capable of application to the analysis of airborne colliery dust, it has a serious disadvantage in that it is expensive of dust, 1 g. being required for an analysis. The tendency of the cyclo hexane to evaporate ffom the mull during operation of the spectrometer and the considerable difficulty of obtaining a cell having a constant film thickness also lead to inaccuracies in the execution of the method.

It was therefore decided to try to apply a pelleting technique to the problem of mounting the solid under examination in the infra-red beam of the spectrometer. In this method a small amount of the finely ground solid under examination is thoroughly mixed with dry finely ground potassium bromide and the mixture is then compressed into a transparent pellet. Since potassium bromide is transparent to infra-red radiation over the usual frequency scan of an infra-red spectrophotometer the pellet may therefore be mounted in the light beam of the instrument and the spectrograph of the dispersed solid may thus be recorded directly. This obviously overcomes the difficulties of solvent evaporation and of superimposition of the spectra of the substances forming the dispersion medium upon the spectrum of the dispersed solid under examination. In addition much smaller quantities of solid are required to carry out a spectrographic examination.

The potassium bromide pelleting technique was developed simultaneously by Stimson and O'Donnel in America (38) and by Schiedt and Reinwein in Germany (39). Many other workers have since applied the technique to problems of both organic and inorganic analysis which were indissoluble, or difficult to absolve, by other

means. For example, Browning, Wiberley and Nachod applied the technique to the estimation of atropine and scopolamine in mixtures of these two alkaloids (40), while Kirkland applied the method to the estimation of quartz in quartz-cristobalite mixtures (34) in the inorganic field.

In the present work a press similar to that developed by Ford and Wilkinson (41) was employed. The press components were fabricated in stainless steel and specially hardened surfaces were provided for the die and anvil. The $\frac{1}{2}$ in. diam. die and anvil were enclosed in an outer evacuable casing and a $1\frac{1}{4}$ in. B.S.F. screw mounted on a suitable cast-iron platform acted as ram upon the die plunger. Effort was applied manually to the ram by means of a ratchet wrench approximately eighteen-inches in length. The practical difficulties of producing optically clear potassium bromide pellets using this type of press (41) are described in detail by Ford and Wilkinson.

To manufacture a pellet the anvil was located in the inner casing, a suitable quantity of potassium bromide mixture which had been previously ground to a particle size of less than 1 μ was then measured into the die opening, and the die and die plunger were replaced. This assembly was then placed in the outer casing and the potassium bromide mixture was evacuated in situ for at least a minute to remove traces of water vapour. The press was then mounted under the ram and the ram was tightened up to the die plunger and slackened off once or twice, to ensure that an even layer of powder was obtained on the anvil. Finally maximum bodily effort was applied to the wrench and the die pressure was allowed to remain for five minutes before slackening off. The potassium bromide in the presswas continuously evacuated during the pressing process and the vacuum was only finally released when the ram had been slackened off. The inner casing was then removed and the anvil was dislodged from its location in the die opening by dealing the free end of the die plunger a sharp blow on a wooden surface. The potassium bromide crystal, which was normally optically clear, was then carefully

removed from the polished surface of the die.

Assuming a maximum effort on the part of the operator of 150 lbs. at an effective radius of 1 ft. and a screw efficiency of 5%, a die pressure of approximately 10 tons/in^2 is obtained using this press. However much higher pressures, of the order of 500 tons/in^2, would be available using a suitable hydraulic press (42) and, in addition, much easier disc removal would be achieved if the press were of the split-casing type (34).

Owing to the difficulty of weighing solids accurately, into the press a number of small brass moulds were made and the ground potassium bromide mixture was tamped into these and then transferred to the press. Three such moulds were made, one being 0.5 in. diam and 0.1 in. deep, one 0.5 in. diam and 0.05 in. deep, and one 0.3 in. diam and 0.05 in. deep. Crystals were made using each of these three moulds, but it was found that only the crystals produced using the smallest mould were of sufficiently high quality for use in this investigation; these crystals were also of the minimum thickness convenient for handling. Crystals of greater thickness and of sufficiently high quality would however be obtainable if a hydraulic press capable of high die pressures were employed.

Mixtures of 10 g. of potassium bromide and 2 g., 0.6 g., 0.3 g., 0.2 g., 0.1 g. and 0.05 g. of quartz were prepared. These mixtures were each ground in a mechanical agate mortar for 15 hours in order to reduce the particle size to less than 1-u and, finally, about 1 g. of each of the mixtures was ground for five minutes in a small high frequency ball mill. Using the smallest of the three moulds for measuring purposes, about eight identical pellets were then made from each of the above mixtures.

In order to, as nearly as possible, cover the path of the infra-red light beam of the spectrophotometer used it was found necessary to employ four crystals. These crystals were mounted in a $2\frac{3}{4}$ in. x $1\frac{5}{8}$ in.

x $\frac{3}{8}$ in. brass block slotted to fit into an existing liquid cell holder. Since the average diameter of the potassium bromide crystals was 0.506 in., four holes arranged, as nearly as possible, to cover the light beam, were drilled in this block for half the thickness of the block to a diameter of 0.515 in., and for the remaining thickness to a diameter of 0.495 in. thus providing a ledge for the potassium bromide crystals to rest upon. The four selected pellets were, in practice, dropped gently into their respective holes with the block held horizontally and a thin 2in. x $\frac{3}{8}$ in. brass strip, bent into the shape of a circle, was pressed gently home after each of the crystals, so that the latter did not topple from their proper location when the block was returned to a vertical position.

Using this holder crystals made from each of the six mixtures of varying quartz content were examined in the spectroscope. The spectrographs obtained showed that Beer's Law was obeyed, even approximately, only at very low quartz concentrations and that a maximum "peak depth" for the absorption maximum shown by quartz at a wavelength of 12.5μ was obtained using crystals containing approximately 1% of quartz. Below this concentration much poorer absorption was obtained, while at higher concentrations light scattering led to a lower general transmittance with a consequently impaired spectrograph.

It was accordingly decided to employ crystals containing approximately 1% of the dust under analysis when estimating quartz contents and to measure the absorptions obtained at a wavelength of 12.50μ, since only at this wavelength does free silica show a sharp absorption band which is relatively unaffected by the superimposed spectra of other minerals commonly found in mine dusts. It was again found convenient to employ the precautions previously taken to allow for the daily variations in the sensitivity of the instrument employed and, with dusts containing less than 50% of quartz, an aliquot portion of

the dust was again mixed with an equal weight of quartz before pelleting, as it was noted that the accuracy of the method fell off considerably where the quartz content of the dust under analysis was less than 50%.

The standard dust samples provided by Dr. Nagelschmidt (24) were first analysed. 10 g. of dry potassium bromide and 0.1 g. of dry dust were weighed into an agate mortar (10 g. of potassium bromide, 0.05 g. of dust and 0.05 g. of quartz in the case of samples containing less than 50% of quartz) and the material was then ground and pelleted in the manner described above. The spectrographs obtained from these pellets were then compared with the spectrographs obtained from similar pellets containing pure quartz (X1072) by comparing the corresponding absorptions at a wavelength of 12.5 μ using the base-line method. The values of the estimated quartz contents of these standard samples obtained from duplicate analyses by the method described above, by the variation of Dolinsky technique developed by Prentice and by the Shaw-Skinner semi-micro gravimetric method, together with the actual quartz contents, are given in Table 16. The samples were all ashed prior to analysis in order that the results should give an indication of the accuracy likely to be obtained when using ashed colliery dust rather than rock dust.

Table 16

Comparison of Methods for the Estimation of Free Silica

Sample	Actual Content of Free Silica (%)	Estimated Content of Free Silica (%)		
		Gravimetric	Infra - Red	
		Shaw-Skinner	Dolinsky	Pot-Bromide
X 1876	0.0	1.2	3.0	0.0
X 2431	0.0	0.5	7.3	0.0
X 2478	0.0	0.5	0.0	0.0
X 2479	14.0	17.0	19.9	11.9
X 2480	48.4	49.0	54.7	48.7
X 2043	66.7	66.0	61.1	65.5
X 1072	100.0	100.0	100.0	100.0
Maximum Error (%)		3.0	7.3	2.1
Standard Deviation (%)		1.3	5.4	1.8

The results given in Table 16 show that the infra-red spectrographic method employing potassium bromide pellets is comparable in accuracy to the Shaw-Skinner semi-micro gravimetric method for the purpose of determining the free silicia content of rock dusts. In calculating the standard deviations of the two infra-red analytical methods employed allowance was made for the following factors. Firstly, that sample X1072 was used as a standard for comparison with the other samples and the figure of 100.0% reported as being the estimated free silicia content of this sample is not therefore a true result, and, secondly, that small negative values were in fact obtained for the estimated free silica contents of a number of dusts. While the latter results have no physical significance and were therefore reported as being zero in Table 16, the actual values obtained must naturally be

taken into account when estimating the accuracy of the method.

The free silica contents of three samples of airborne coal mine dust were then estimated using the pelleting method described above. In this case the actual silica contents of the samples were, of course, unknown and the accuracy of the infra-red method for this application was judged by conducting parallel estimations using the Shaw-Skinner semi-micro gravimetric method. The infra-red analysis was implemented in a manner exactly similar to the method described above, the samples being ashed prior to analysis to obviate interference from the numberous absorption bands due to organic matter (33) present in the airborne colliery dust, and a mixture of 0.05 g. ash, 0.05 g. quartz and 10 g. potassium bromide being used for pelleting, as the free silica content of airborne coal mine dust ash is almost invariably less than 50%. The results obtained are given in Table 17 and it will be seen that good agreement is obtained between the infra-red and the gravimetric method, taking into account the considerable experimental error involved in both methods.

Table 17

Comparison of Methods for the Estimation of Free Silica in Airborne Colliery Dust

Sample	Estimated Free Silica Content (%)	
	Shaw - Skinner	Infra - Red
3.K.6	2.1	1.3
3.K.7	1.0	0.7
3.K.8	12.3	9.9

Since the absorptions shown by the potassium bromide pellets were found to obey Lambert's Law the accuracy of the method obviously depended upon consistency in the thickness of the pellets produced. The pellets formed were actually found to have a thickness between 13.2 and 15.1 in x 10^{-3} with an average thickness of 14.2 in x 10^{-3} and a standard deviation in thickness of 0.6 in x 10^{-3}, while the mass of the crystal varied from 0.1196 g. to 0.1357 g. with an average mass of 0.1269 g. and a standard deviation in mass of 0.0052 g. Obviously a good deal of the inaccuracy noted must proceed from this source and much of this inaccuracy could be eliminated by employing an internal standard (43) such as potassium thiocyanate which does not have absorption bands in the region of 12.50 μ wavelength.

While inaccuracy, due to variations in crystal thickness may thus be eliminated, error will nevertheless proceed from the following sources, namely : (a) presence of particles of greater than 1 μ in size, (b) incomplete dispersion of the solid under analysis in the potassium bromide, (c) weighing and transfer errors resulting in variation of concentration, (d) instrumental errors and (e) errors due to the superimposition of the spectra of the colliery dust ash constituents; other than quartz, which display absorption maxima in the region of 12.50 μ wavelength. It is thought that errors due to the first four causes can be reduced to a satisfactorily low level, but, while little interference from superimposition of the spectra of colliery dust constituents other than quartz was detected in the present investigation, more detailed work with a more sensitive instrument may show that allowance (44) for dilluents, such as kaolinite and muscovite which show weak absorption bands in the region of 12.50 μ wavelength, would improve the accuracy of the method.

Conclusions

While the Shaw-Skinner semi-micro gravimetric method is effective when applied to airborne colliery dusts in yielding data on their free silica content of reasonable accuracy and practical value, its execution

is very time-consuming, about 20 man-hours being required for a duplicate determination, and this factor is a serious hindrance in work of this sort.

An infra-red spectrographic method in which the dust under analysis is dispersed before examination in a potassium bromide pellet has been suggested above as an alternative to the gravimetric method. This method appears to be of comparable accuracy to the Shaw-Skinner method and requires only about four man-hours for the duplicate determination. The method, however, is in need of further investigation before complete reliance can be placed upon it, and it is thought that such investigation would further increase its accuracy.

Alternatively the x-ray diffraction method developed by Nagelschmidt (24) may be used to rapidly determine the free silica contents of the dusts. This method, however, requires highly developed and expensive equipment.

ESTIMATION OF THE TOTAL SILICA CONTENT OF DUSTS

Introduction

The pathogenicity of an airborne dust containing free silica is largely dependent, from a silicosis viewpoint, on the proportion of the silica content of the dust which is present in the free or uncombined form.

The "silica solubility" of the dust is greatly reduced where a large proportion of the silica content of the dust is present in the combined form as silicate. The reduced solubility of the quartz content of high silicate dusts is in fact due to a small amount of aluminium hydroxide released by the mineral silicates which are generally in the form of kaolins or micaceous minerals, which goes into solution in the water to a sufficient extent to deposit on the quartz particles, coating their surface. It is also thought that the reduced pathogenicity of high silicate dusts is due to this cause.

On account of this effect it was considered advisable to determine the total silica content of each airborne dust sample in addition to estimating its free silica content, so that the silica present in each dust sample in the combined form could readily be obtained by difference. The problem of determining the total silica content of a substance is much less complicated than the problem of determining the free silica content, as no distinction need, obviously, be made between the two types of silica present in the dust.

Gravimetric Method

King's semi-micro gravimetric technique (45), which is fully described in Appendix A, was adopted as the standard method for estimating the total silica content of the airborne colliery dusts examined. The method consists essentially of a fusion of the sample with sodium carbonate, after which the silica is precipitated from the fusion products, filtered, and finally estimated by evaporation with hydrofluoric acid.

It was found that when the colliery dust was ashed prior to the fusion step, which decreased losses due to spurting of the melt, a reproducibility of within ± 0.5% in the silica content was obtainable. Each estimation was carried out in duplicate and the results of this survey are reported in the final section of the thesis.

King's semi-micro gravimetric method was both reliable and reasonably accurate, having an estimated accuracy of about ± 1%, when applied to the determination of the total silica contents of airborne colliery dusts, but it was also, however, both rather expensive of dust, about 0.5 g. of dust being required for an accurate duplicate analysis, and rather time-consuming, about 12 man-hours being required for the duplicate determination.

Colorimetric Estimation

An attempt was therefore made to analyse three airborne coal dust samples (3.K.6., 3.K.7. and 3.K.8) using a rapid colorimetric method which would be economical in dust. An adaptation of the molybdenum blue method used by Clelland (46), described below, was employed.

The following solutions were made up :-

(a) Standard Silica Solution :

0.0392 g. of commercial sodium silicofluoride was dissolved in distilled water and the solution was made up to 500 ml. and stored in a polythene bottle. This solution was equivalent to a solution of 0.025 g. silica in 1 litre of distilled water, taking a purity factor of 99% for the sodium silicofluoride.

(b) 5% Ammonium Molybdate Solution

"Analar" ammonium molybdate (6 g.) was dissolved in a little distilled water. The solution was then filtered through a Whatman's No. 542 paper and made up to 100 ml. 6N sulphuric acid (20 ml.) was then slowly added to the solution with constant stirring.

(d) Reducing Solution

"Analar" sodium sulphite (60 g.) and "Analar" hydroquinone (10 g.) were dissolved in distilled water and the solution was made up to 500 ml. with distilled water.

The intensity of the blue colour produced when using this method was measured by an E.E.L. colorimeter using a red filter (Ilford No. 608). The colorimeter was calibrated as follows. Solutions containing 25 ml. of borate buffer and 1,2,3,4,5,6,7,8,9, and 10 ml. of standard silica solution were placed in cellulose acetate ("Lustercid") tubes and made up to 43 ml. with distilled water. 5% ammonium molybdate (2 ml.) was added to each tube, the solution was stirred for 30 seconds and the yellow colour allowed to develop for five minutes. Reducing solution (5 ml.) was added and the solution stirred for 30 seconds. The blue colour was allowed to develop for 30 minutes and its intensity was then measured by the colorimeter.

A calibration graph of colorimeter reading against silica concentration was then plotted, in which concentrations of silica were expressed as mg. silica/50 ml. of total solution.

The total silica contents of the airborne colliery dusts were then estimated as follows. About 0.02 g. of dust was weighed out accurately into a platinum crucible, ashed, and intimately mixed with 0.45 g. of sodium borate and 2.79 g. of boric acid (≡ 250 ml. of borate buffer solution). The whole was heated, gently at first to drive off water of crystallisation and then vigorously until fusion was complete. Before cooling the crucible was tilted to allow the mixture to spread up the sides in order to facilitate getting the mass into solution. The crucible was then cooled and the contents were taken into solution by gently heating the crucible containing warm distilled water on the water bath. The contents were then filtered into a 250 ml. graduated flask and the extractions repeated until the fused mass was completely in solution. After

washing the filter funnel with warm water, the solution in the flask was allowed to cool and then made up to the mark.

Portions of this solution were now tested for iron and phosphate (45) but these were found to be absent in every case. Thus, while a number of inorganic anions and cations interfere with the molybdenum blue colour reaction (47), few of these are left in a water soluble form after a borate fusion.

A few ml. of the test solution was then measured into a "Lusteroid" test tube containing 25 ml. of borate buffer solution, made up to 43 ml. with distilled water and the molybdenum blue colour was developed and its intensity measured using the .E.E.L. colorimeter as described above. The silica content of the solution was then found using the calibration graph and thence the silica content of the dust under analysis was calculated. The volume of test solution taken depended on the silica content of the dust and was adjusted to give a concentration of 0.1 to 0.2 mg. SiO_2/50 ml. in the final solution.

The accuracy of a colorimetric method very similar to that described above has been shown to be $\pm$ 1.75% (48). In contrast with the gravimetric method, which requires about 0.5 g. of dust and 12 hours for a duplicate determination, the colorimetric method described above can be successfully conducted on only 0.02 g. of dust and only about four man-hours are required for the duplicate determination.

Comparison of Methods

The results obtained using both the above colorimetric method and King's semi-micro gravimetric technique on three airborne colliery dust samples are given in Table 18.

Table 18

Comparison of Methods for the Estimation of Total Silica in Airborne Coal Mine Dusts

Sample Reference	Estimated Total Silica Content (%)	
	Gravimetric	Colorimetric
3.K.6	9.8	11.1
3.K.7	9.5	9.9
3.K.8	31.3	33.1

The results given in Table 18 show agreement within the limits of accuracy of the methods employed, although the predominantly higher values for the total silica contents of the dusts given by the colorimetric method may have been due to the fact that the purity factor taken for the "technical" grade sodium silicofluoride used in calibration was too high. However agreement is sufficiently good to show that the colorimetric method described above is a fairly accurate means of estimating the total silica content of airborne colliery dusts. Further, since it involves less time and requires less dust than the gravimetric technique, it is to be preferred in investigations into the silicosis hazard of airborne colliery dust, as in this type of work large sampling errors are involved and much time is required in order to collect a small amount of dust underground.

ESTIMATION OF THE CARBON AND CARBONATE CONTENTS OF DUSTS

Introduction

In many coal mines pulverised limestone is used when rock-dusting to allay the danger of coal-dust explosions. It was therefore interesting to discover whether large quantities of this limestone dust were normally entrained from the roadways so that the typical airborne dust in the colliery contained a substantial proportion of limestone. Consequently the carbon and carbonate contents of two typical airborne colliery dusts were determined using established methods of fuel analysis, in order to discover whether these dusts contained significant quantities of limestone.

Results

The carbon contents of both samples were determined by high temperature combustion in a stream of pure oxygen, followed by absorption and weighing of the carbon dioxide formed, while the carbonate contents were determined by the volumeteric method of Sinnatt and Harrison (49). The results of these determinations together with the total silica contents of the two samples employed are given in Table 19.

TABLE 19.

Carbon and Carbonate Contents of Dusts

Sample	Ash (%)	Carbon (%)	Carbonate (%)	Total Silica (%)
C.4.	52.9	34.7	1.1	25.6
3.K.5.	28.0	48.2	0.4	13.1

Conclusions

Since it could be calculated from the results of the combustion determinations that, on the dry ash free basis, sample C.4. contained 81.1% carbon and 5.2% hydrogen while sample 3.K.5. contained 67.3% carbon and 4.3% hydrogen and since the carbonate contents of these samples are only respectively 1.1% and 0.4%, it is obvious that the dusts consist essentially of coal particles with mineral silicates as

dilluent and that only a very small proportion of limestone or other mineral carbonates are present.

RESULTS AND CONCLUSIONS

Results

(a) Pilot Samples

Ten pilot samples were first obtained from nine different Scottish pits, by continuous collection underground over a period of days. The sources, times of collection and weights of these samples are given in Table 20, while the results of their analyses are reported in Table 21. Only one of the samples obtained (E.F.1.) was in any way suspect. This sample contained pieces of coal well over 1 cm. in size, which were reputedly due to shotfiring, and therefore only the portion of the sample passing a 200 mesh B.S. sieve was subjected to analysis. However the facts that an unusually high proportion of fine material of less than 1 μ in size and that an unusually high proportion of silicate material were present in the sample, as seen in Table 21, tend to confirm that the large pieces of coal found in the sample did indeed originate from shots being fired in the immediate vicinity of the collector.

The figures reported in Table 21 as "Mass % $< 5\mu$ were determined from particle size analysis of the re-dispersed dust under the Vickers Microscope using a 4 mm. objective as no comprehensive thermal precipitator surveys were carried out during the collection of these pilot samples. The figures reported as "Mass % $< 1\mu$" were also determined by examination of the similarly redispersed dust under the electron microscope using a magnification of 2,600 X and therefore both of these figures will contain a considerable error due to presence of agglomerates.

The electron diffraction patterns obtained appear merely to show that a degree of surface crystallinity was present in the samples and it would appear, particularly in the case of sample E.F.1., that diffraction patterns were obtained not only from the quartz content of

the dust, but also from various silicate minerals present in the dust.

Since workers would not normally be continuously exposed to the airborne dust of the colliery but would work in a series of successive shifts the purpose of these pilot samples was to estimate the spread of results likely to be obtained in these investigations, rather than to estimate the health hazard of the dust to workers exposed to its effects. It will be seen that both the particle size distribution and the silica contents, with the possible exception of sample E.F.1. are of the same order for all the samples. Further, where the free silica content of the dust is seen to increase above the average value for the samples this is generally accompanied by a similar increase in the total silica content of the dust.

It is also seen that there is good agreement, at least in a qualitative sense, between the results obtained using the optical microscope and those obtained using the electron microscope.

It may be noted also that the two samples collected continuously in the same section of the same pit in fairly close succession (3.K.1., and 3.K.2.) are very similar both in particle size distribution and in chemical composition. This appears to indicate that the average dust composition at one point in a particular pit does not normally alter rapidly.

(b) Shift Samples

In order that the typical dust to which various workers would normally be exposed could be examined, samples collected entirely during one of the three shifts (cutting, stripping and brushing) were obtained from Cardowan No. 1 Colliery and from Kingshill No. 3 Colliery. These samples were collected in the return airway in order to estimate the health hazard to face-workers but, in addition, one sample was collected continuously in the intake airway in Cardowan No. 1 Colliery during collection of the shift samples in order to estimate the health hazard to workers in this airway.

TABLE 20

Sample	Source and Dates Collected	Weight (g.)
3.K.1.	Kingshill No. 3 Colliery, Shotts, at No. 7 Mid Coal Section, from 20/2/56 to 25/2/56	2.0
C.i.	Cardowan Colliery in Right Return Airway at No. 2 East Section; from 25/2/56 to 2/3/56	13.2
3.K.2.	Kingshill No. 3 Colliery, Shotts at No. 7 Mid Coal Section; from 12/3/56 to 17/3/56	1.0
1.K.1.	Kingshill No. 1 Colliery, Shotts, at Section 4, West B; from 15/3/56 to 17/3/56 and from 19/3/56 to 29/3/56	0.7
L.V.1.	Lady Victoria Colliery, Newtongrange, in Return Roadway of Newbattle No. 4 Section. Sample collected for one week ending 28/3/56	3.6
P.1.	Plean Main Coal, Alloa Area, at Peeler Section; Collector ran for 5 days ending 18/4/56	16.0
E.F.1.	This sample was collected somewhere in the East Fife Area and contained pieces over 1 cm. in size. It was therefore suspected. Times of collection unknown	5.5
M.1.	Mauchline Colliery, West Ayr Area; collector ran for five days ending 20/4/56	2.0
V.1.	Valleyfield Colliery, Dunfermline, at Dunfermline Splint Section; collector ran for five days ending 23/4/56	0.7
L.1.	Lugar Works, Cumnock, Ayrshire. Times of collection unknown	1.0

TABLE 21

Sample	Mass % < 1 μ	Mass % < 5 μ	Electron Microscopy	Ash (%)	Free Silica (%)	Total Silica (%)	El
3.K.1.	1.4	36.1	Very fine. Almost all < 10 μ	31.5	4.4	15.4	M
C.1.	0.2	19.2	Mainly large 1 - 30 μ with a considerable number of fine particles < 3 μ	32.5	5.3	12.0	I l H g
3.K.2.	0.9	24.1	Fine. Mostly < 10 μ	31.2	4.0	14.5	M
1.K.1.	1.4	26.7	Fine. Mostly < 10 μ	44.8	3.2	21.2	F f R
L.V.1.	1.1	30.2	Fine. Mostly < 10 μ	39.8	5.4	20.8	F s g p o
P.1.	0.2.	20.2	Mainly large 1-30 μ Comparatively little fine material	17.2	4.4	9.0	R c o a g
E.F.1. *	3.3	51.8	A few particles > 30 μ but mainly 1 - 20 μ with considerable fine material < 1 μ	41.8	1.0	21.3	F c o
M.1.	0.7	39.2	Mainly 1 - 10 μ. Very little greater than 20 μ rather few fine particles.	61.4	12.7	30.7	F c o
V.1.	0.2	13.8	Mainly very large 1 - 50 μ. Much less than usual < 3 μ.	16.5	2.7	7.6	Fa cr He gr &
L.1	0.2	20.8	Largely 1 - 10 μ with a few particles of about 20 μ	29.4	4.7	16.0	Fa cr Ri ma hex gr

* Indicates suspect sample. Only the fraction passing a 200 me
B.S. sieve (< 200 μ) was subjected to the processes of analy

The sources of the Cardowan shift samples are given in Table 22 together with the mean dust concentrations existing during their collection and their individual weights. The results of analysis of these samples are given in Table 23. The results of the shift sampling investigation in Kingshill No. 3 Colliery are given, in similar fashion, in Tables 24 and 25.

A comprehensive thermal precipitator survey was carried out in both pits during collection of the above samples. The figures quoted for "Mass % < 5μ" in Tables 24 and 25 were therefore obtained using thermal precipitator slides selected to be representative of the mean dust concentrations during collection and performing particle size analysis under the Vickers microscope using a 4 mm. objective. The Mass % < 1μ" figures were calculated from the mean dust concentration figures, supplied by the National Coal Board and given in Tables 22 and 24, together with the results of the corresponding particle size analysis obtained using the Vickers microscope. In this way advantage was taken of the higher resolution of the Beck instrument employed by the National Coal Board in their routine dust counts. The figures given for "Mass % < 1μ" and "Mass % < 5μ" should therefore be free from dispersion error and substantially free from sampling error, although some error may occur in the former figure due to the limits set by the ultimate resolution of the optical microscope.

The specific surface values reported in Tables 23 and 25 were obtained by the low temperature nitrogen adsorption method using either liquid oxygen or liquid nitrogen as coolant. The figures reported in Table 23 were obtained using liquid oxygen in the cold bath and these figures may well be in considerable error due to the limitation place upon the relative pressure obtainable in the glass apparatus employed. The specific surface values obtained for the Kingshill shift samples were however determined using liquid nitrogen as coolant which reduced the experimental error to a more acceptable level.

Considerable difficulty was again experienced in interpreting the significance of the electron diffraction results, but good qualitative agreement was again noted between the results of the examinations under the electron microscope and under the optical microscope.

It will be noted that the particle size distributions and silica contents of the samples are again all of the same order, although minor changes do occur from pit to pit and from shift to shift. It will be seen on examination of the results obtained from the sample collected in the intake airway, where the mean dust concentration is lower, that many of the larger particles of coal dust appear to have settled out leaving a rather higher proportion than usual of fine particles. In addition, however, a number of fairly large particles have also become airborne and these probably originated from low energy sources such as may have been created by repair work in the intake roadway.

At a considerably later date a further series of shift samples was obtained from Kingshill No. 3 Colliery and the sources, weights and the results of the analysis of these samples are given in Tables 26 and 27. These samples were obtained with the main object of developing more rapid methods of chemical analysis, but the results obtained by the standard methods of gravimetric estimation used throughout the remainder of the work are reported in Table 27 in order to avoid confusion due to variations between results obtained by different methods of estimation.

Comprehensive thermal precipitator data for the period of operation of the collectors were not available in the case of the second series of shift samples. Consequently the "Mass $\%<5\text{-}\mu$" figures reported in Table 27 were calculated from particle size analysis of the redispersed dust, while the Mass $\%<1\text{-}\mu$" figures were calculated from the mean dust concentrations given in Table 26, in the Sections in which the dusts were collected together.

TABLE 22

Weights and Sources of Shift Samples from Cardowan

Samples were collected over six working days in Cardowan No. 1 Colliery at No. 3 East Section.

Sample	Source & Time of Collection	Mean Dust Concentration (p.p.c.c.)	Weight (g)
C.2.	In Return Road during Cutting Shift	(0.5 - 5 μ) 981 (1 - 5 μ) 286	2.2
C.3.	In Return Road during Stripping Shift	(0.5 - 5 μ) 585 (1 - 5 μ) 244	5.5
C.4.	In Return Road during Brushing Shift	(0.5 - 5 μ) 1225 (1 - 5 μ) 568	11.7
C.5.	In Intake Road continuously	(0.5 - 5 μ) 626 (1 - 5 μ) 123	1.4

Analyses of Shift Samples from Cardowan No. 1 Colliery

Sample	Mass % < 1 μ	Mass % < 5 μ	Electron Microscopy	Specific Surface $cm^2/g.$	Ash %	Free Silica (%)	Total Silica (%)	Electron Diffraction
C.2.	0.4	30.7	Fine. Mainly 0.5 - 10 μ with occasional rectangular shaped particles up to 40 μ x 10 μ	37,900	27.3	3.1	13.1	Highly crystalline Diffraction as rings of spots. Crystals appeared to be small
C.3.	0.4	18.8	Rather finer. Nearly all 0.5 to 10 μ. Many chain-like aggregates of small particles present. Large particles sharply outlined, but also some cotton wool like particles	55,800	14.8	3.0	6.5	Diffraction as rings of spots. Crystals appeared to be small.
C.4.	0.4	30.1	Similar, but some larger material of the order of 20 μ present.	35,600	52.9	7.0	25.6	Large particles highly crystalline Diffraction as rings of spots. Crystals appeared to be small.
C.5.	1.2	13.5	Large proportion of particles < 1 μ but also some large particles of the order of 30 μ. Many of fine particles arranged in chains.	27,400	17.3	2.6	7.6	Diffraction as rings of spots. Crystals appeared to be small.

Table 24

Weights and Sources of First Series of Shift Samples from Kingshill

All the samples were collected by means of five H-J samplers operating simultaneously in Kingshill No. 3 Colliery. The samples were collected consecutively using the same five collectors in the Return Road of No. 7 Mid Coal Section.

Sample	Time of Collection	Mean Dust Concentration (p.p.c.c.)		Weight (g.)
3.K.3	During four consecutive Cutting Shifts	(0.5 - 5 μ) (1 - 5 μ)	333 164	1.2
3.K.4	During four consecutive Stripping Shifts	(0.5 - 5 μ) (1 - 5 μ)	824 381	2.5
3.K.5	During three consecutive Brushing Shifts	(0.5 - 5 μ) (1 - 5 μ)	512 272	2.5

Analysis of First Series of Shift Samples ffom Kingshill No. 3 Colliery

Sample	Mass% <1 μ	Mass % <5 μ	Electron Microscopy	Specific Surface $cm^2/g.$	Ash (%)	Free Silica (%)	Total Silica (%)	Electron Diffraction
3.K.3	1.3	59.0	Mainly in range 1 - 20 μ. Quite a high proportion of particles > 10 μ	43,850	34.4	5.6	17.5	Highly crystalline. Hexagonal cross-grating patterns. Large crystals seemed to be present
3.K.4	0.7	56.3	Nearly all in range 0.5 - 10 μ Many particles of cotton-wool like appearance	60,000	28.4	2.9	12.8	Highly crystalline. Rings of spots. Crystals seemed to be small
3.K.5	0.2	22.5	Mainly in range 1 - 20 μ. Many chain-like aggregates. Large particles pointed and of regular outline	36,450	28.0	3.4	13.1	Highly crystalline. Hexagonal cross-grating patterns. Large crystals apparently present

Table 26

Weights and Sources of Second Series of Shift Samples from Kingshill

The samples were obtained using three collectors operating simultaneously in Kingshill No. 3 Colliery at Nos. 2 and 3 South Sections for the periods indicated.

Sample	Source & Times of Collection	Mean Dust Concentrations (p.p.c.c.)		Weight (g.)
3.K.6	Collected during Cutting Shift over 35 working shifts	(0.5 - 5 μ) (1 - 5 μ)	632 297	3.75
3.K.7	Collected during Stripping Shift over 10 working shifts	(0.5 - 5 μ) (1 - 5 μ)	311 99	5.5
3.K.8	Collected during Brushing Shift over 15 working shifts	(0.5 - 5 μ) (1 - 5 μ)	431 268	4.95

Table 27

Analysis of Second Series of Shift Samples from Kingshill No. 3 Colliery

Sample	Mass % < 1-μ	Mass % < 5-μ	Specific Surface ($cm^2/g.$)			Ash %	Free Silica (%)	Total Silica (%)
			Miscroscopic	Lea & Nurse	B.E.T.			
3.K.6	0.7	20.7	6,170	11,000	52,100	21.8	2.1	9.8
3.K.7.	1.0	13.7	4,870	10.020	53,000	20.2	1.0	9.5
3.K.8	0.5	16.5	3,750	8,350	68,000	57.8	12.3	31.3

with the appropriate particle size analyses. Both sets of figures are therefore subject to a considerable error due to incomplete dispersion of the dust.

The values given for the specific surfaces of the dust samples in Table 27 were obtained by three different methods. Firstly by calculation from the results of optical analysis of the redispersed dusts, secondly by duplicate determinations using the air permeability method of Lea and Nurse and, finally, by duplicate determinations using the low temperature nitrogen adsorption (B.E.T.) method employing liquid nitrogen in the cold bath. It will be noted that, whereas the results obtained using the air permeability method agree as to the relative size of the samples with the results obtained using the microscopic method, such agreement is not shown by the results of the B.E.T. determinations. It would appear therefore that the low temperature nitrogen adsorption method measures a specific surface value which is less dependent upon particle size than the value determined by an air permeability method.

The silica contents of the dusts are of the same order as before and where, in sample 3.K.8., the free silica content rises above the average value for airborne colliery dusts, this increase in free silica content is largely counteracted by a corresponding increase in the total silica content of the dust.

A comparison of the average ash contents and silica contents of shift samples, averaged on the basis of the weights of such samples which would be collected over an equal time interval, and the chemical composition of corresponding continuously collected samples are given in Table 28.

Table 28

Comparison of Corresponding Shift and Integrated Samples

Sample	Ash (%)	Free Silica (%)	Total Silica (%)
C.1	32.5	5.3	12.0
Average Values for Cardowan Shift Samples	39.2	5.4	18.8
Average of 2.K.1 and 3.K.2	31.4	4.3	15.1
Average Values for First Series of Shift Samples from Kingshill	29.2	3.6	13.8
Average Values for Second Series of Shift Samples from Kingshill	35.7	5.8	18.4

The results obtained appear to show that, while the dust composition may alter considerably from shift to shift, the average dust composition at any point in a given colliery remains fairly constant over considerable periods of time. Since the second series of shift samples obtained from Kingshill No. 3 Colliery were obtained after a considerable lapse of time from a different section of the colliery, it is not surprising that the average values obtained from this series of samples agree less closely with the values for the corresponding integrated samples than do the average values obtained from the first series of shift samples which were obtained shortly after the integrated samples in the same section of the colliery

Conclusions

The results obtained are not sufficiently numerous to be statistically significant. They do however serve to show that the average free silica content of airborne colliery dust is low, exceeding 10% of the total in the case of only one (M.1) of the twenty samples examined. Further, where a dust has an unusually high free silica content a correspondingly high total silica content is generally found, so that the pathogenic effect of the free silica is reduced. From this point of view little justification has been found for the theory that coal miners' pneumoconiosis is a modified form of silicosis.

These investigations have also shown that if it is intended to carry out an extensive programme of dust sampling from which a statistical survey could be made it is very advisable to restrict the tests carried out on the dust samples obtained underground to those which can be carried out in a fairly short period of time using only a small quantity of dust. In this way both the sampling time underground and the time spent in testing in the laboratory may be reduced and results which bear statistical significance may be obtained in a shorter period of time. While methods are given in the main body of the work whereby the free silica and total silica contents of airborne colliery dust samples may be determined with sufficient accuracy in a reasonable period of time using only small quantities of dust, no alternative has been found by the writer to the method of conducting an accurate thermal precipitator monitoring of the collection point followed by microscopic analysis, as a means of accurately determining the particle size distribution of the airborne colliery dust. This provides another strong reason for limiting the sampling time underground and applying only tests which require a very small quantity of dust.

In view of the fact, however, that all of the colliery dust samples obtained consisted predominantly of coal macerals, as might be expected, much more fruitful results might well be obtained by examining these

constituents of airborne colliery dusts than by a prolonged statistical survey of mineral or siliceous constituents of the dusts.

Suggestions for Future Work

In any future survey designed to associate the incidence of coal miner's pneumoconiosis with the silicosis hazard of the airborne colliery dust causing the disorder, the writer suggests that only the following fairly rapid tests should be applied.

(a) Particle-size analysis. This may be carried out by means of a detailed examination under a suitable optical microscope of a small number of thermal precipitator slides selected to be representative of the mean dust concentration during collection. It is, of course, also necessary to carry out a preliminary count upon all the slides obtained from the thermal precipitator survey carried out while the collector is in operation. This test is consequently time consuming and may require about 20 man-hours for the average sample.

(b) Free-Silica Content. This may be determined either by the x-ray diffraction technique developed by Nagelschmidt (24) or by the infra-red spectroscopic method described in the text of this thesis after the necessary confirmation and, possibly development of the method has been carried out. If the spectroscopic method is employed about 0.5 g. of dust and four man-hours will be required for the duplicate determination.

(c) Total-Silica Content. This may be determined by the molybdenum blue colorimetric method described in the text. If this method is employed approximately 0.02 g. of dust and four man-hours will be required for the duplicate determination.

Thus, if two workers were allocated to test (a) and one worker was allocated to tests (b) and (c), this means that a group of three workers, in a suitable laboratory operating a 35 hour week, could complete approximately 15 samples per month or 180 samples per annum. This annual total represents about the minimum number of samples from which

a statistical survey could be made and in such a survey parameters derived from the results of the three tests above to represent the silicosis hazard of the dusts collected could be compared with incidence figures derived from the available certification records of the pits from which the samples were obtained.

Approximately 0.75 g. of airborne colliery dust would be required to carry out tests (b) and (c) and an average collection period of approximately forty hours would probably be required underground to collect this quantity of dust. Thus four samplers would be required to devote their time completely to the tasks of collecting the dust samples underground and carrying out a complete thermal precipitator survey on the airborne dust clouds from which the samples were collected.

It is therefore apparent that a considerable expenditure of labour will be required both in the laboratory and underground before a statistical correlation of the silicosis hazard of airborne colliery dusts and the incidence of coal miners' pneumoconiosis may be attempted. This is the case even when labour-saving methods of analysis using small quantities of dust are employed.

In the writer's opinion some work should also be done in attempting to correlate the proportions of the various coal macerals present in the airborne colliery dust with the incidence of pulmonary disease, perhaps along the lines suggested by Evans (3). Since coal forms the major part of all colliery dusts it seems logical that attention should be directed towards this constituent. Such an investigation would require the collection of large quantities of airborne dust, at least in the initial stages until methods of analysis had been developed, but, at least in the preliminary stages, it is probable that such factors as particle size distribution could be safely neglected.

APPENDIX A

The Estimation of Free Silica in Airborne Dusts

The Shaw-Skinner Semi-Micro Method (27)

Reagents

Hydrochloric acid dilute	2.5% by volume. 2.5 ml. of conc. acid are diluted to 100 ml. with distilled water
Hydrochloric acid, dilute	5% by volume. 5 ml. of conc. acid are diluted to 100 ml. with distilled water
Sulphuric acid, dilute	25% by volume 25 ml. of conc. acid are diluted to 100 ml. with distilled water.
Sulphuric acid, dilute	10% by volume. 10ml. of conc. acid are diluted to 100ml. with distilled water
Lunge Solution	37 g. of anhydrous sodium carbonate and 10 g. of caustic soda are dissolved in distilled water and diluted to a volume of 1,000 ml. and stored in a waxed glass or preferably, plastic bottle.
Hydrefluoric acid	40% acid

Method

0.15 g. of the sample, after drying at 105° C, for at least 1 hour, is heated to boiling with 9 ml. of 2.5% hydrochloric acid in a 50 ml. platinum basin, covered with a watch glass, preferably of resistance glass (Pyrex or Hysil). A 3 in. (7.5 cm.) porcelain dish may be used provided the glaze is in good condition. This treatment is to remove any carbonates. After allowing the dish to cool, the liquid was decanted down a glass rod into a 15 ml. centrifuge tube which is centrifuged for 15 minutes at 3,000 r.p.m. The clear supernatant liquid is drawn off through a tube whihh has been drawn out to a capillary, the end being

turned up to avoid disturbing the sediment in the tube. (With care, the liquid may be decanted off down a rod, since the sediment is tightly packed). The solid matter is then washed back into the dish with the minimum amount of water, and the dish is placed on the boiling water bath and the contents evaporated to dryness. After cooling, 6 ml. of 25% sulphuric acid are added and the uncovered dish is heated until fumes are just visible. This operation should take about 45 minutes and the temperature of the contents of the dish should not exceed 200°C at any time. There are several ways of doing this, e.g. a sand bath, the temperature of which has been carefully adjusted in a parallel experiment beforehand, or, a method which has been in use for some time is to support the dish on a perforated plate and then blow air at a temperature of 180 - 200°C upwards through the plate.

After treatment with sulphuric acid, the dish is allowed to cool and then 30 mls. of water are added, the liquid stirred and centrifuged as above, the tubes will have to be filled two or three times. The residue is then washed back into the dish, the liquid evaporated to dryness, and the sulphuric acid treatment is repeated. When all the liquid has been transferred to the centrifuge tube the dish and its contents are washed with 5 ml. of water, which is then centrifuged. The purpose of this wash is to remove as much as possible of the sulphuric acid and thus reduce the amount of Lunge solution needed in the next stage of the work. After the wash liquid has been centrifuged and discarded the residue is returned to the dish and the liquid evaporated to dryness. To the dry residue is then added 1 drop of methyl red indicator, followed by Lunge solution drop by drop until the indicator changes colour. The dish should be covered during this operation since loss can occur due to effervescence. After neutralisation, 9 ml. of Lunge solution are added in excess and the covered dish is heated until the liquid boils. After cooling, the supernatant liquid is centrifuged, the clear liquid discarded, and the residue is washed back into the dish and evaporated to dryness.

15 ml. of conc. hydrochloric acid are then added to the covered dish, and the dish is heated until its contents have boiled for 5 minutes, and after cooling, the contents of the dish are diluted with 15 ml. of water, which can with advantage be used for washing the cover glass. The liquid is then decanted, centrifuged, the residue returned to the dish, and after evaporation to dryness, the residue is again neutralised with Lunge solution. When neutral, 4.5 ml. of Lunge solution are added and the contents of the dish are heated to boiling and after cooling, the liquid is decanted, centrifuged, and the residue washed back into the dish. After evaporation to dryness the residue is treated with 6 ml. of conc. hydrochloric acid and boiled for 5 minutes. When cold, 6 ml. of water is added and the liquid filtered through a small (7 cm.) No. 540 Whatman paper. The residue in the dish is washed twice with 5% hydrochloric acid the washings being added to the paper then the solid matter in the dish is completely transferred to the paper with the aid of a jet of water, the dish being cleaned finally either with a small rubber "policeman", or better with a small piece of cotton-wool twisted round the end of a glass rod. The cotton-wool can be detached easily from the rod and added to the paper. On ignition it leaves no weighable residue. The paper is washed four times with water and allowed to drain. It is then transferred to a weighed platinum crucible, which is covered with its lid and heated in an oven at 105°C. until the paper is dry. The covered crucible is then placed in the front of a muffle furnace which is heated to 800°C. at its centre for 10 minutes when it is moved to the centre of the furnace and ignited to constant weight (Residue A). The ignited residue is finally treated with 6 drops of 10% sulphuric acid and 5 ml. of 40% hydrofluoric acid and treated on a boiling water bath until all the volatile matter has gone. The crucible is then heated on a hot plate until all the redisual sulphuric acid has fumed off, when the crucible is again ignited at 800°C. to constant weight.

Calculation

The residue (A) remaining after the ignition following the last hydrochloric acid treatment consists of the free silica and some undecomposed silicates, which are assumed to be potash felspar. The loss in weight caused by the hydrofluoric acid treatment is due to the volatilisation of the free silica and the silica combined in these silicates. The final residue therefore consists of the non-siliceous portion and after ignition is in the form of alumina. On the macro scale it would be possible to estimate this and obtain a figure for the amount of felspar actually present. On the semi-micro scale however this is not possible, but the amount of alumina multiplied by 2.01 gives a very close estimate of the amount of felspar.

The calculation therefore is as follows :-

If A is the weight of total residue and B is the weight of residue remaining after the hydrofluoric acid treatment, then the percentage of free silica present in the material is equal to (A - 2.01 B) 100/wt. of material taken. To correct for loss of quartz by solution in alkali the final figure is multiplied by 100/92.

i.e. $$\frac{(A - 2.01\ B)}{\text{Wt. of mat. taken}} \times 108.6$$

Notes

It must be borne in mind that this method, as do all the chemical methods for the determination of free silica, consists of a series of operations designed to remove from the material under examination all minerals except the quartz, and, as already stated the attack of the reagents on the quartz is corrected for. Therefore to obtain reliable results the conditions must be reproducible and this can only be done if strengths of reagents, quantities, times of heating etc. are all strictly controlled.

Boiling

The liquid in the dishes was considered to be boiling when drops began to condense on, and fall from the watch glass. This is especially important in the conc. hydrochloric acid treatments. Considerable bubbling, due to liberation of carbon dioxide occurred on immediate heating, but after about 1 minute the liquid became still and proper boiling began after about another minute. Prolonged boiling was always avoided.

Interruption

The whole cycle of operations cannot be finished in one day, so that when work had to be stopped, care was taken that the residues in the dishes were left in the dry state.

Mechanical Losses

In such a long series of operations as those described, mechanical losses can be very high. Dishes were kept covered as much as possible and great care was taken to see that decantations were done cleanly. Washing the residues back into the dishes from the centrifuge tubes also required care.

Reagents

Volumes were measured carefully with a graduated pipette for those less than 10 ml. and a narrow diameter measuring cylinder for the others. The 40% hydrofluoric acid was measured in a plastic cylinder.

The basins were heated for the boiling operations on a sand bath, but for evaporation a boiling water bath was used.

The Estimation of Total Silica in Airborne Dusts
The King Semi-Micro Method (45)

Method

An amount of dry airborne dust is taken which may be expected to yield 5 - 50 mg. silica and carefully weighed in a platinum crucible of 10 - 20 ml. capacity. The dust is then ashed at 750°C for one hour in a muffle furance and the ash, after cooling is intimately mixed with four times its weight of sodium carbonate. The mixture is carefully "smoked off" and heating continued until a clear liquid melt is obtained. The cooled contents of the crucible are dissolved in water on the steam bath. Conc. hydrochloric acid is carefully added until the mixture is acid to methyl orange, and 3 or 4 ml. extra added. The mixture is evaporated to dryness on the steam bath, and heated for one hour at 105°C in the oven to dehydrate the silica. The residue is moistened with a few drops of water and hydrochloric acid, and again heated for one hour at 105°C.

The dehydrated silica is separated from the other constituents of the residue by bringing the latter into solution with dilute hydrochloric acid. The residue is moistened with conc. hydrochloric acid and the crucible three-quarters filled with water. The mixture is warmed on the steam bath and stirred with a glass rod. When solution appears to be complete, the crucible is removed from the bath and allowed to stand for a few minutes for the silica precipitate to settle.

Filtration of the silica is accomplished without removing it from the crucible by means of a filter stick. In this way it is possible to complete all the operations involved in the analysis in the original vessel without transferring the precipitate. This makes for greater accuracy in the method by avoiding the possibilities of error involved in transference. Filtration by sucking off the filtrate and washing is, moreover, faster than filtration by gravity. As a filtering medium,

filter paper pulp shaken up with water, or powdered anthracene is suitable. The latter is easily eliminated by mild heating, whereas paper must be destroyed by ignition. The filtering medium is packed tightly into the cavity formed at the flared end of the filtering apparatus. A piece of fine rubber suction tubing connects the filter stick to a small suction flask. Suction is applied by mouth to a piece of rubber tubing carrying a pinchcock attached to the side arm of the flask.

The filter stick is held so that its filtering surface is just below the level of the liquid in the crucible, and the filtrate sucked off under mild suction. The crucible is filled again with warm dil. HCl and the precipitate stirred, allowed to settle, and the supernatant again sucked off. Washing is repeated once with dil. HCl and twice with water. The precipitate is finally sucked dry in the bottom of the crucible.

The plug of filtering medium is dropped out of the filtering apparatus into the crucible by pushing the inner tube of the apparatus (the filter stick) a few mm. through the rubber collar which attaches it to the outer tube or jacket. Particles of silica adhering to the glass are washed into the crucible and any liquid in the crucible is now evaporated on the water bath. The crucible is dried in an oven, ignited at 750°C for one hour in a muffle furnace, cooled in a disiccator and weighed. HF(5 ml.) is added and a few drops of H_2SO_4. It is then ignited, cooled and weighed. The loss in weight on treatment with HF is taken as the weight of silica.

APPENDIX B

NOTES ON THE PATHOGENSIS OF PNEUMOCONIOSIS

Effect of Dust on the Human Respiratory Tract

To understand the pathogenesis of silicosis it is necessary first to appreciate the effect upon the human respiratory tract of inhaled dust laden air. The air breathed by man travels eventually to the lungs which are non-symmetrical organs, encased in the chest, permitting interchange of gas between the blood and the external air. They communicate with the nose and mouth through the trachea, or windpipe, and are more or less exposed to the action of atmospheric impurities, both particulate and gaseous.

Certain mechanisms do however exist to protect the lungs from accumulation of such foreign matter. The nose is guarded by a coarse filter of hair through which inspired air is drawn into the trachea and particles of 15 to 25 μ are likely to be retained here. Behind this is a series of tortuous passages with moist walls which trap many smaller particles. Thus many particles greater than 5 μ in size travel no further than the nasal passages or the back of the throat. Inspired air from the nose and mouth travels through the pharynx and trachea, the latter being about 1 to 2 cm. in diameter and 10 cm. long. The trachea branches into bronchi, which in turn branch into narrower bronchioles leading finally to the terminal alveoli, or air sacs, which compose the lung. Air is drawn into and expressed from the lung partly by the movement of the diaphragm and partly by movement of the rib-cage or thorax.

Particles which pass into the upper respiratory tract may be arrested in a viscous mucous layer which covers the surface of the pharynx, trachea and bronchi. This viscous layer is in fact a film of mucus covering a lower non-viscous serous layer in which beat minute vibratory hairs or cilia, causing the upper layer to move slowly toward the mouth, from which the foreign matter may be either expectorated or

swallowed. This mechanism is adequately described in a paper by Policard (50).

Particles that succeed in passing these barriers and penetrate to the terminal air spaces of the lung may adhere to the alveolar walls. The presence of the particle in this environment generally causes sufficient irritation (51) to lead to hypertrophy and hyperplasia of the cells of the alveolar tissue. This leads to the production of a different type of cell, known as a phagocyte, which may ingest the mineral particle. This cell is capable of amoeboid motion, owing to flowing of its own cytoplasm, and it may therefore move slowly through the alveolar ducts and bronchioles to the bronchi and hence as before. Another route is, however, open to such "dust-cells", as phagocytes containing dust particles are known; they may travel into the connective tissue spaces of the bronchiolar sheath to a special drainage system known as the lymphatics. Lymphatic spaces and vessels are very numerous in the lung, especially in the connective tissue sheaths of the bronchi and arteries, in the interlobular walls, and under the pleura. In the normal lung the dust-cells are swept away in the lymphatic vessels by the flow of the lymph and finally come to rest in a number of sedimenting basins known as the lymph nodes.

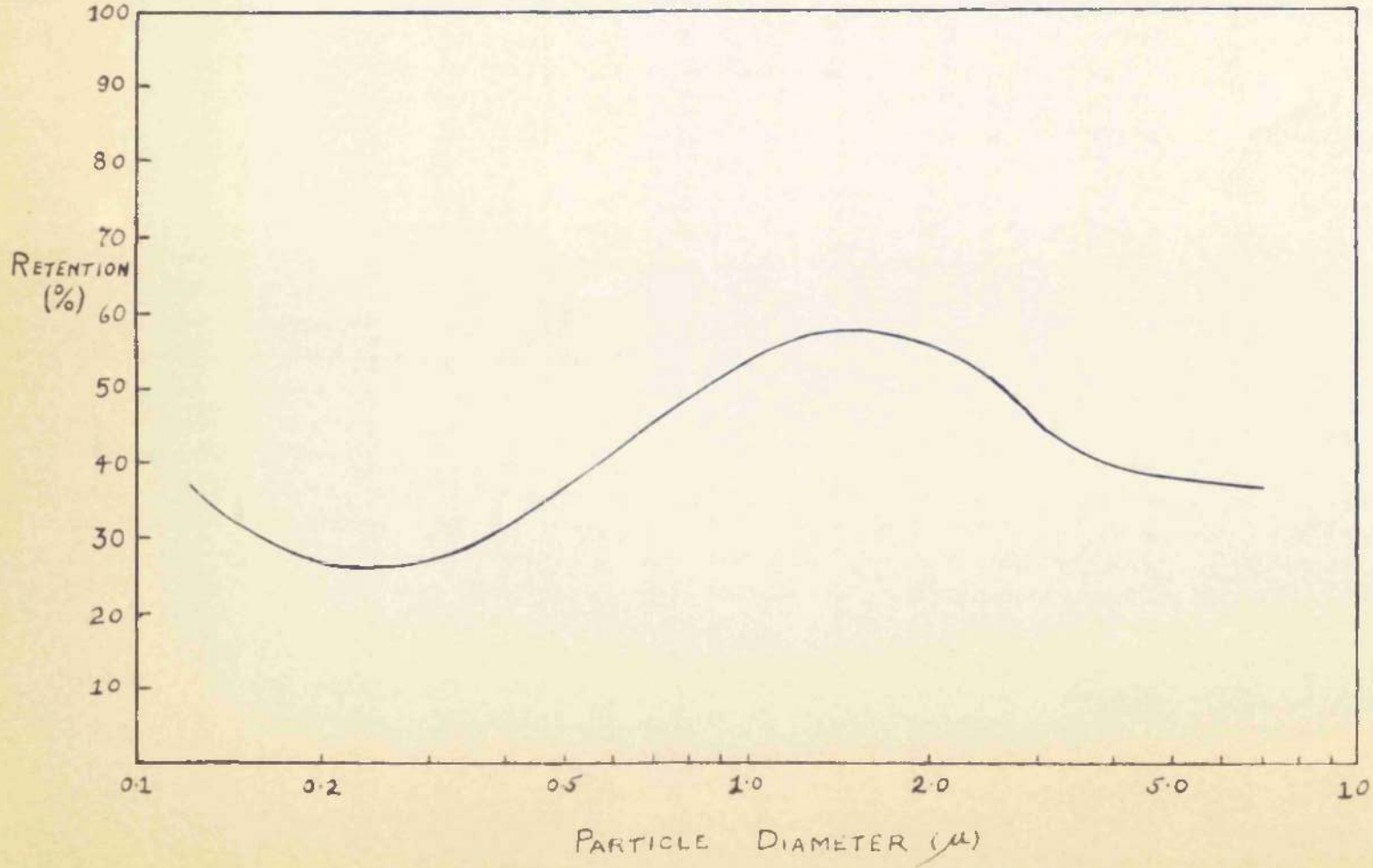
One factor, however, has not been considered in the foregoing summary of the defences of the respiratory tract against dust, and that is the percentage of dust which is exhaled. It is possible that the theory of probability could be applied to determine the quantity of dust which escapes contact with the bronchial tree, but at present there is no information on this. However, it is obvious that small particles of colloid dimensions will easily escape in the exhaled air.

It will be seen that under normal conditions the human lung possesses a very efficient mechanism for ridding itself of inhaled dust, and dust is expelled from the healthy lung either by the respiratory tract or the lymphatics. This mechanism, however, is easily upset, and slight alterations in the condition of the ciliated epithelium or the

Fig 14

Alveolar Retention of Particles of Unit Density

(after Davies)



circulation of lymph are sufficient to interfere with it, for example irritation of the goblet cells of the brochial epithelium can lead to an undue production of mucus which then envelopes the cilia and prevents their beating, or mechanical damage to the lymph channels, or infection may produce stasis of the lymph. In this condition a second mechanism comes into play and the dust entering the lung is fixed, agglomerated, and rendered harmless by the protein residue remaining after autolysis of the dust cell. This, however, is not a real cleansing process and the presence of the dust mechanically impairs the function of the arterial sheaths by obstructing the flow of lymph and producing stasis. Thus this mechanism is protective at first, but later, when there is a considerable accumulation of dust, pneumoconiosis begins, which is essentially a disease due to the mechanical presence of large amounts of foreign material in the lung.

Any dust particles which penetrate to the final air-sacs, or alveoli, of the lung, and are retained there, thus obviously constitute a danger. Fig. 14 showing the alveolar retention curve for an average human lung is taken from a review paper by Davies (52), who points to the substantial agreement between a number of investigators using different experimental methods. It will be seen that particles in the size range 0.5 to 5-μ are mainly retained in the lung and it is chiefly this size range towards which attention must therefore be turned when evaluating the health hazard due to any dust cloud encountered in practice. While particles of less than 0.2-μ are also largely retained in the lung, there is considerable doubt as to their pathogenic effect, the lower limit of dust size at which fibrotic effect ceases being, in fact, only very roughly established.

Theories on Silicosis Development

Early workers thought that dust was harmful chiefly because of its physical presence in the lungs, and that the particles, on account of their hardness and sharpness, produced a microscopic wounding, or trauma, of the delicate tissues. Quite apart from the fact that it is difficult

to conceive of mechanical trauma due to particles of less than 5 μ, it also became obvious that this theory could not entirely explain the pathological effects of dust. Finely divided silica dust rapidly produces extensive lung disease, while carborundum dust, which has extremely sharp edges, does not produce the typical silicotic nodule (53). The practice of stone dusting in mines to prevent explosions was also found to decrease rather than increase the incidence of lung disease. These facts led to some doubt as to whether the physical presence of the dust itself could alone produce the pathological effect observed. Attention was therefore turned to the possible existence of toxic substances in the dust which were released into the lung fluids.

This reasoning led Gye and Kettle (54) to propose their well-known solubility theory of silicosis which held that silica dust was harmful in the lungs not only because of its mechanical presence but also because the particles released a certain amount of silicic acid which dissolved in the surrounding fluid with irritating effect upon the engulfing lung cells. Policard later confirmed this irritating effect of dissolved silica (55) and showed that cells poisoned by this substance became "mummified" and preserved from the normal processes of protein degeneration. Kettle also showed in his later experiments that quartz dust covered with a thin layer of iron oxide (56) has much less effect than the uncoated dust in producing silicotic nodules in animals. In tests of this sort the dust is normally introduced to the animal's lung by intra-tracheal injection (57) or, better, by subjecting the animals to an artificially created dusty atmosphere (58).

The solubility theory is by no means the only theory which has been advanced to explain the pathogenesis of silicosis. Zrenner in a review article (59), suggests that the irreversible action taking place in the silicotic lung is caused by a combination of mechanical trauma and chemical action. Some effect is also thought to be caused by exchange of bases between the mineral particle and the surrounding tissue, basic

ions such as calcium, sodium and potassium going into the environment from the spaces in the mineral lattice, and being replaced by water molecules or hydroxyl ions. Two consequences result, alkalinisation of the medium and hydration of the mineral particle. Alkalinisation of the lung fluids would increase the solubility of any quartz present and therefore, presumably, its degenerative effect. The actual process of base exchange is also thought to result in hypertrophy of tissue. The second consequence of exchange of bases, namely hydration of the particles, is also interesting in its effects. This hydration process has also been confirmed by petrographic examination of particles extracted from the lung, when it has been found that the superficial lattice of the particle may have been altered to a depth of 0.2 μ, and thus a particle of 0.4 μ in size may have been completely changed. This molecular alteration of the particle is thought by some investigators to render the particle harmless and, since the same "weathering" process occurs on exposure to rain, moist air etc., this explains the accepted innocuousness, from a silicotic point of view, of natural dusts such as river sand and desert sand.

However, although the theories outlined above cannot be discounted, by far the greatest weight of experimental evidence supports the solubility theory; and this will therefore be selected for further expansion.

The Solubility Theory

It is perhaps surprising that quartz should be harmful to the lung. Its chemical inertness is a matter of common knowledge and it is frequently thought of as being one of the most insoluble of substances. It is true that a large crystal of quartz left for a long period in a vessel containing water will scarcely dissolve at all, but if the large quartz crystal is first reduced to a fine powder and then introduced to the water significant amounts of silica may be shown to be present in solution.

The amount of silica in solution may at the present time be estimated accurately by the silico-molybdic acid technique (60) although even this method is liable to include in the figure obtained a very small amount of polymerised silicic acid which is molybdate reactive. The lung fluid has a pH of about 7.4, and this may be simulated by using Ringer's solution, instead of water, for solubility tests. King, Mohanty, Harrison and Nagelschmidt carried out solubility tests on flint samples of different particle sizes using Ringer's solution (61). Their results are given in Table 29 and it will be seen that the amount of silica dissolved, for equal weights of flint (a natural form of free silica) in equal volumes of Ringer's solution, is related to the size of the particles.

TABLE 29

Silica solubility of flint dusts of different size.

Particle Size (μ)	0.5	0.5 - 1	1 - 2	2 - 4	4 - 8
Solubility (mg.SiO_2/100 ml.)	13.6	13.4	13.1	8.9	5.1

Flint, granite and opal are rocks which are rich in free silica, and dust from these rocks rapidly causes silicosis, while rocks such as shale and slate often contain silica chiefly in the combined silicate form and give a dust by no means so prone to generate lung disease. The "silica solubility" of such dusts is also much lower.

As mentioned previously, much work has been done on estimating the pathogenicity of mineral dusts in animals. In general the results have agreed with the bulk of industrial experience regarding the health hazard created by airborne mineral dust of various sorts.

Quartz dust, for example will rapidly produce nodules in the lungs of animals, with a superficial appearance very similar to that of the human silicotic nodule. Pure silicate dusts, on the other hand,

including sericite, produce only a very mild reaction. Acid-treated sericite, surprisingly, causes a rather large amount of fibrosis, but this is probably due to the increased solubility conferred to the sericite dust by the acid treatment. On closer microscopic examination, animal silicotic lesions are seen, however, to be not so well organized and to contain much less dense collagen fibres than the human lesion. The appearance of animal silicotic lesions, developed over a long period, does however become progressively closer to that of the human silicotic nodule.

Mixed dusts of free silica and silicates give lesions in the lungs of animals which are always intermediate between those produced by quartz on the one hand, and by silicates on the other. If much quartz is present, as in a high quartz sandstone, silicotic nodules will result; but if the silicates predominate, as in mica, kaolin or hornblende, the tissue reaction is mild and like that produced by the silicates themselves.

This effect may well be explained by the depressing effect which shale dust has upon the solubility of quartz.

In a mixture of kaolin, mica and quartz, for example, one might expect the amount of silicic acid dissolved to be conditioned by the most soluble constituent of the mixture, quartz, and that in presence of excess of the mixed powder the solubility would approach that of quartz taken alone. This, however, is not the case (62) and admixture of stone dust with powdered quartz will depress the solubility from 140 mg./l. to about 10 mg./l.

The shale-dust component which depresses the solubility of quartz is, in fact, a small amount of aluminium hydroxide which is sufficiently water-soluble to deposit on the quartz particles, producing a thin layer over their surface. This effect may be demonstrated by adding powdered aluminium, alumina or aluminium hydroxide to quartz dust, when its

silica solubility will be reduced from about 150 mg./l. to about 10 mg./l.

It is not certain whether these depressions in solubility do in fact explain the depression in silicosis caused by the presence of stone dust in air containing quartz particles, but they do, at least, form a very suggestive parallel.

Experiments with animals have also demonstrated the retarding effect exerted by the dust of aluminium or its oxide upon silicosis development. A significant fact revealed by these investigations is that the aluminium dust must be administered continuously in order to exert its therapeutic effect, otherwise the alumina is apparently lost by dissolution in the lung fluids leaving the quartz free to promote fibrosis in the normal way. Thus Denny, Robson and Irwin (63) were able to demonstrate the preventive effect of aluminium dust upon silicosis development in rabbits using a dusting technique in which the animals breathed aluminium daily, while Belt and King (64) were unable to confirm these results using intra-tracheal injection. Denny, Robson and Irwin found that the addition of 1% of aluminium dust to the quartz dust resulted in an effective inhibitive action upon silicosis production in the animals, and their findings have more recently been confirmed by other workers (58).

While it would appear that constantly administered aluminium or alumina dust would act as a suppressant upon silicosis production, no convincing evidence has been put forward to indicate that such dust may be used with curative effect.

Aluminium and alumina dust have both been tried as prophylactics for silicosis. In Denver, Colorado, a well controlled experiment was conducted with developed silicotics who breathed alumina dust. Control subjects breathed fresh air through the same apparatus. All the men expressed personal opinions that their condition had improved, including the control subjects, but this subjective improvement was completely

unsupported by any scientific evidence either from X-ray or clinical examination.

Thus, while the practice of stone dusting in coal mines does, in fact, decrease the incidence of lung disease, the removal of the health hazard created by airborne dust more probably lies, not in the introduction of further dust even if that dust be antidotal, but in the suppression of the dangerous dust already present.

The Silicotic Nodule

Human silicosis presents a very definite histological picture, particularly in advanced cases, where nodules having a "ball of twine" appearance develop within the lung. These nodules consist of a good deal of fibrous scar tissue which holds the dust content of the lesion. The dust is distributed within the nodule in a definite pattern, there being a densely packed central core of dust particles surrounded by an almost vacant zone which corresponds to the densest of the whorled collagen fibres, and this is again followed by a halo of dust corresponding to the periphery of the nodule.

Other Factors influencing Silicosis Development

Pure silica exists at room temperature in four different modifications : quartz, cristobalite, tridymite and fused silica or vitreosil. The first three are crystalline but vitreosil is an amorphous fused solid or glass. Quartz is the only modification which is thromodynamically stable, but none of the metastable forms show any measurable tendency to invert to quartz at normal temperatures.

Since quartz crystals have an asymmetric structure they may exist in either the "d-" or "l-" form. Experiments indicate that either stereoisomer is equally effective in promoting fibrosis in animals.

Similar animal tests, however, show that there is a marked difference in the pathogenicity of the various crystalline forms (61). While cristobalite appears to promote fibrosis to only a slightly greater or

equal extent to quartz, tridymite appears to be very much more lethal and vitreosil appears to be considerably less lethal than quartz. This result seems to indicate that the crystal structure of the pure silica does influence the tissue reaction.

This explanation appears quite satisfactory for the lower activity shown by vitreosil which has a disordered type of structure, but it appears rather remarkable that the small structural difference between tridymite and quartz or cristobalite should produce an almost threefold increase in pathogenicity, since all these crystalline structures are composed of SiO_2 tetrahedra sharing oxygen corners, differing only in the arrangement of the tetrahedra in space and in the bond angle made between the two silicon atoms and the oxygen atom bound to both. The non-silicosis producing felspars are also very similar to quartz in crystalline structure, so that it seems unlikely that crystal structure alone can have so great an effect upon fibrotic properties.

It has already been shown that the particle size of quartz dust influences both its ability to penetrate to the terminal air sacs of the lung and the amount of silicic acid which a given weight of such dust may liberate into solution. If solubility alone, therefore, is the only factor controlling the development of fibrosis in the lung, equal weights of quartz dust of varying particle size should increase in pathogenic effect with decreasing particle size. On the other hand, on the same hypothesis, if varying weights of the various particle size ranges are administered, such that a dose of equal surface area is given in each case, then the pathogenic effect of these various batches of dust of different particle size should be the same.

King, Mohanty, Harrison and Nagelschmidt (65) performed experiments of the above type on rats in which flint dust of different particle size ranges was given to rats by intra-tracheal injection. Their results are quoted in Tables 30 and 31.

TABLE 30

Constant amount series (50 mg. flint per rat)

Flint size (μ)	Silica solubility (mg./100 ml.)	Surface per rat (cm^2)	Maximum stage of fibrosis	Reached after (months)	Minimum time to stage (months)			
					2	3	4	5
4 - 8	5.1	170	2	9	9	-	-	-
2 - 4	8.9	350	3	10	5	10	-	-
1 - 2	13.1	750	5	9	1	5	7	9
0.5 - 1	13.4	2,000	5	7	1	2	3	7
0.5	13.6	3,000	5	5	1	1	1	5

TABLE 31

Constant - Surface Series

Flint size (μ)	Wt. of dust per rat (mg.)	Silica solubility at constant area (mg./100 ml.)	Minimum time to fibrosis stage (months)		
			3	4	5
4 - 8	199	4.1	8	-	-
2 - 4	100	4.2	1	4	6
1 - 2	42	4.6	1	4	5
0.5 - 1	17.5	2.1	1	7	10
0.5	8	4.1	1	10	-

It will be seen from Table 30 that fibrotic effect is indeed closely related to silica surface, but closer examination, (Table 31) reveals there to be a range of maximally fibrogenic particles in the region of 1 to 2 μ, and, from the design of the experiment, it is obvious that this is not due to a maximum concentration of silicic acid being released into solution.

Dempster and Ritchie (22) have shown that quartz particles obtained by grinding contain a relatively highly soluble outer layer which may be removed by repeated buffer extraction and can be regenerated by further grinding or polishing. King, Mohanty, Harrison and Nagelschmidt (66) have conducted animal experiments to test the pathological significance of these observations. Two sets of quartz samples were prepared, one by leaching with Ringer's solution and the other by etching with hydrofluoric acid. The untreated quartz samples served as controls.

Both treatments reduced the silica solubilities of the samples to about 10 per cent of their original value. The sample leached with Ringer's solution was found, however, to be equally as effective as its control in promoting fibrosis, while the sample etched with hydrofluoric acid was even more pathogenic than its control.

This type of evidence, together with the evidence given in Tables 30 and 31, may justify modification in our conception about silica solubility and its relation to fibrogenesis, although it may be that the high solubility layer of the treated quartz samples was regenerated in the lung.

Another interesting fact which should be taken into account in considering the validity of the solubility theory is the acute toxic effect of colloidal silica. Dale and King (67) found that 1 - 2 mg. of colloidal, 20 Å (0.002 μ) silica caused rapid death in mice, while 30 mg. of silica of respirable dimension (0.1 - 5 μ) were required to cause death. The acute toxic effect of the colloidal silica was not decreased by addition of alumina, dyes, or protein, which substances are strongly adsorbed on silica of respirable size.

A Recent Concept of the Mechanism of Silicosis

King (68) suggests a possible mechanism of silicosis in which both colloidal silica and dissolved silicic acid play a part. "Fine quartz particles release silicic acid into solution in a liquid or in the liquid contents of a cell. Some of the silicic acid escapes into the blood, and is carried away to be excreted, other silicic acid molecules polymerise to colloidal dimensions, and become fixed on the protoplasm of the cell. Colloidal silicic acid is a protein precipitant, and its action in precipitating some of the protein of the engulfing cell may be the cause of the typical fibrotic response which is always caused by the presence of free silica particles in tissues. The quartz particles, however, must be of fairly definite size range. They must not be too small, like 20 Å silica, or they will produce an acute toxic effect. If they are too big, no appreciable dissolution will take place. The formation of silicotic nodules is a slow chronic phenomenon. It appears that to produce them silica particles must be small enough to liberate slowly, and over a long time, soluble silica into solution from their surfaces in sufficient amount to produce a chronic local irritative effect; and must not be so small that they will quickly and completely dissolve and be either carried away or produce only an acute local effect, which will lack the continuous stimulus of constantly released colloidal silicic acid. It may be this prolonged irritative, or stimulating, effect of constantly released colloidal silica which is responsible for the formation of the fibrous scar tissue of a silicotic nodule."

"Belt described the structure of the silicotic nodule as a core of densely packed fibres containing numerous doubly refractive particles of silica, surrounded by a sheath of fibre. Micro-incineration revealed a dense halo of fine silica at the periphery, but a space almost vacant of silica between the periphery of the fibrous sheath and the core. This structure strongly suggests a diffusion, outward from the central

deposit of particles, of silicic acid, much of which becomes fixed on protoplasmic constituents in a zone slightly outside and surrounding the core, where micro-incineration reveals it as a multitude of very fine amorphous particles, easily seen in dark-field illumination, but not visible with the refracting microscope. It has been suggested elsewhere that particles of quartz in the lung release silicic acid which has special biological properties. This biologically active silica may be nothing other than polymerised silicic acid or colloidal silica."

Origins and Constitution of Airborne Coal Mine Dust

In general, dust clouds in coal mines may be formed in three ways, firstly by evaporation of mist or fog particles containing dissolved or suspended solids, secondly by the blowing up of dust which has settled, and thirdly by mechanical disintegration of a solid.

If a liquid containing dissolved or suspended solids is dispersed as a mist, subsequent evaporation of the liquid will produce dust particles. In mining, particles of this type are produced at the release ports of a central water-feed machine drill and in other ways.

Dusts blown up by air currents tend to consist of large rather than small particles since the latter are more firmly held than the former by cohesive forces to the surface on which they have settled. Accordingly, large particles may be raised by an air current, but small particles which may have settled on them may not be separated from them. Fine particles can of course be blown up by a sufficiently powerful air current, but the finer the particles the more difficult it is to do so.

When particles are formed by the mechanical disintegration of a given solid, the average size of the particles produced is, to a first approximation, inversely proportional to the amount of energy expended per unit mass of the solid. This is due to the fact that a solid, like a liquid, may be regarded as possessing a surface tension, so that a definite amount of energy must be expended to produce a new surface.

The actual values to be assigned to the surface tensions of solids are known only approximately and vary considerably from one material to another, and also with the particular surface of the material relative to the crystal axis. As has already been mentioned the crystalline structure of the surface of solids produced by mechanical disintegration is profoundly changed, a surface of irregular structure, or Beilby layer, being formed (22), one of whose properties, by comparison with the normal solid, is a higher solubility.

Thus in drilling with a machine drill, where large amounts of energy are expended upon a small amount of solid, one would expect a very fine dust, while in drilling by means of a hand hammer a very much coarser dust is obtained, owing to the lower energy expenditure on a given amount of solid. Similarly, while considerable quantities of fine dust are produced during blasting operations, very little fine dust is obtained either by shovelling the coal, or tipping it into trucks or hoppers.

Airborne dust in coal mines may, in fact, proceed from several sources, such as mechanical disintegration of the coal, or the non-coal sediments in the seam, or the strata composing the roof and floor of the seam, and also from dust from comminuted coal formed by compressional movements along so-called "slip-planes" in the seam.

A very comprehensive mineralogical survey of such airborne coal mine dusts has been carried out by Evans (69) (2) in various collieries of the South Wales coalfield. He recognised the major types of mineral constituent by means of their refractive indices and uncovered much enlightening information.

In view of its prominence as a pathogenic material, Evans paid particular attention to the mineral quartz. He found that quartz particles found in coal mine dusts could be divided into three main groups.

"Group I" quartz particles are optically clear, or slightly brown tinted, extremely angular particles of quartz which sometimes exhibit

undulose extinction between crossed nicols, indicating strain. Their sharp-edged character is a sign of conchoidal fracture, and Evans therefore suggested that they had been formed by mechanical disintegration of detrital grains in the coal and associated sediments, or from veins or veinlets of secondary quartz. From their nature it would seem that these particles might well be a significant factor in the production of coal miners' pneumoconiosis.

"Group II" particles of quartz are well-rounded and exhibit even extinction between crossed nicols. They are either associated with, or flecked by, coal particles, or coated partially or wholly with kaloinised mineral matter. In all cases they represent eroded grains of quartz released from the parent sediment, mainly coal, without mechanical alteration. Since these particles, in view of their aluminous coating are undoubtedly less chemically active than those of "Group I" they may be of lesser interest than "Group I" particles in estimating the health hazard created by an airborne dust.

"Group III" quartz is only found in specimens which have been incinerated below 400°C. These particles are coagulated aggregates of micro-crystalline matter which refractometrically appear to be silica associated with kaolinised mineral matter. They probably represent colloidal silica in coal or material derived from low-temperature micaceous or ferruginous mineral matter released during incineration. Although this mode of silica is highly soluble in the released state it is probably so inherently bound up with the coal substance as to be of comparatively little significance in promoting the incidence of pneumocconiosis if coal particles are to be regarded as innocuous.

Occasional relatively large (about 30 μ) particles of quartz possessing zoned outer margins are also found in airborne coal mine dusts. It is thought that this form of quartz is due to the rhythmic crystallisation of secondary silica on the primary quartz fragment.

Airborne coal mine dust may, in fact, contain up to about 15% of quartz, although its average quartz content is certainly no higher than 5% but, in addition to quartz, substances belonging to two mineral groups know, respectively, as the micaceous minerals and the "kaolin" minerals are present in airborne coal mine dust which are important on account of their possible suppressing effect upon the pathogenic properties of the quartz particles in the dust.

The micaceous minerals are a complex group of minerals which are principally silicates of aluminium, potassium and sodium, together with silicates of iron, magnesium and lithium. These minerals which are, basically, complex alumino-silicates, vary chiefly in their content of sodium, potassium alumimium and silicon. The chief micas associated with coal measure shales comprise the range of minerals between brammalite ("sodic-sericite") which has an Na_2O content of 5.28%, and illite ("potash-sericite") which has an Na_2O content of 1.05%. Movement through the range of micas from brammalite to illite is accompanied by a slight increase in the silica to alumina ratio. Micas of high soda content are normally found in association with coals of high rank, brammalite being, in fact, first discovered in the associated shales of an anthracite measure.

"Kaolin" minerals in coal mine dusts include minerals such as kaolinite, dickite and nacrite which are essentially $Al_4\ Si O_4\ (OH)_8$ or $(4H_2O,\ 2Al_2O_3,\ SiO_2)$, as well as other hydrated alumino-silicates. The group is made up of crystalline particles as well as micro-crystalline aggregates of kaolinised mineral matter.

Evans identified the kaolinised dust particles (2) in many of his examinations of airborne coal mine dust by treating the dust particles with a solution of an alumina-detecting stain known as "aluminon" (ammonium salt of aurine-tricarboxylic acid) which caused most, if not all, of the constituents of the "kaolin" fraction to acquire a deep red colouration detectable in grains less than 1 μ in size. These probably

represent kaolinised mineral matter which, although possessing an alumina: silica ration similar to that of the more crystalline members of the kaolin group, has not attained their high degree of stability.

Kaolinised matter occurs in widely varying amounts in airborne coal mine dust, either as discrete particles, or coating those of Group II quartz. Since they are capable of releasing alumina under favourable conditions, their presence in quantity may exert a significant depressive effect upon the release of free silica in the lung.

A large number of accessory minerals are also found in airborne coal mine dusts. These include gypsum, anhydrite, dolomite, apatite, ankerite, siderite and rutile, as well as many others, but these substances are found in very variable and generally insignificant amounts.

Evans examined over 400 samples of coal mine dusts and found that coal formed the major part of the dust in every case. He therefore concluded that, irrespective of the manner of working, coal itself is the principal supplier of dust in the mine and suggested that the principal sources of dust inhaled by colliery miners, arranged in order of importance were as follows :

(a) The mechanical disintegration of the coal seam.

(b) The slip dust when present in quantity in the seams.

(c) The strata comprising the roof and floor of the workings as well as from "stone-dusting" where this practice is legally enforced.

Evans found no correlation to exist between the rank of coal being mined and the quartz content of the dust ensuing, but he did note that the average particle size of the coal dust was considerably smaller than that of the mineral dust, and that there was an abundance of quartz particles less than 2 μ in size only where mechanised operations, such as the use of pneumatic picks, were employed.

Coal Miners' Penumoconiosis

Study of these various mineral constituents of airborne coal mine dust would naturally enable its silicosis hazard to be evaluated, but there are several important differences between the pathology of classical silicosis and that of coal miners' pneumoconiosis.

As in classical silicosis one form of coal miners' pneumoconiosis is due to the action of the dust alone, and this is sometimes called simple pneumoconiosis. Another form is due to the combined action of dust and infection. This is infected pneumoconiosis in which tuberculosis is the usual associated infection. An outstanding difference between silicosis and coal miners' pneumoconiosis is that the latter does not have such a disposition as the former to tuberculosis which can be recognised during life. Nevertheless, tuberculosis in a modified and often obscure form is found in a considerable proportion of coal workers dying of pneumoconiosis.

Gough has described the main changes taking place in a coal miner's lung (70) owing to either simple or infected pneumoconiosis. Changes due to dust alone are seen as black spots throughout the lung varying from microscopic size up to about 5 mm. Some of these spots are soft, but others are hard and can be felt as nodules. Although fibrosis has thus occurred at the dust foci the nodules formed vary from those of classical silicosis in that the fibrous tissue is not arranged concentrically, but runs in various directions and often radially. In and around the soft foci the air-spaces are dilated giving a honeycomb appearance, while the hard foci differ only in that there is a central hard core surrounded by a honeycomb of emphysema. This focal emphysema may reach such severity as to cause extensive disorganisation of the lung.

On the background of simple pneumoconiosis there may be superimposed fibrosis due to infection. In the infected form of the disability massive areas of fibrosis occur characteristically in the upper parts of the lung. They are round or elongated and composed of dense black

tissue having the consistency of hard rubber. Sometimes it appears as if masses of coal are embedded in the lung and the affected areas may be as much as 12 cm. in diam. The masses may be uniformly solid or may have in them areas of liquefaction, the fluid present in the cavities being inky black. Although tuberculosis is only positively indentified in about a third of such lungs, the fact that the fibrosis occurs in the sites of predilection for chronic tuberculosis, strongly suggests that tuberculosis always plays a part, but that in some instances the infection is dormant or has died out. In the lungs showing massive fibrosis there are also nodules which are larger than those of simple pneumoconiosis, being up to about 1 cm. in diam. They usually occur near the massive fibrosis, but may be widespread in the lung. They are solid rather than honeycombed, and emphysema is less common about these infected nodules than around the simple nodules.

The degree of disability resulting from either type of miners' pneumoconiosis will depend on the amount of lung in which function has been lost or impaired. This may be due to areas of lung being replaced by fibrous tissue or due to emphysema. Massive fibrosis is compatible with respiratory efficiency provided that the non-fibrosed part of the lung is not emphysematous. Characteristically, however, massive fibrosis in the upper parts of the lungs leads to emphysema in the rest of the lung. This in turn affects the heart and increases the disability.

Various theories have been expounded to explain the pathogenesis of coal miners' pneumoconiosis. One such theory regards the lung disease of coal workers as a modified form of silicosis and this interpretation is supported by the fact that coal in its natural state always contains silica and airborne dust in coal mines, as has been mentioned, contains this mineral together with various other minerals usually originating from associated rock strata. However, disability and fatal lung disease has been found to occur in mines where the dust has a low silica content and, as been pointed out, there are also significant differences in the pathology of the two diseases.

In view of the typically low silica content of airborne coal mine dust, it has been suggested that development of lung disease is due rather to the quantity of dust inhaled by the miner rather than to the silica content of such dust. The fact that several very dusty coal mines have incidences of lung disease well below the average tends to disprove this theory however.

Thus, while it is apparent that coal miners' pneumocooniosis is caused by dust, there is no very definite scientific information as to which constituent of the dust is primarily effective in promoting the disease. Since coal predominates in airborne coal mine dust Evans investigated the actual coal macerals to determine their possible part in promoting changes in the lung tissues. He suggested that the weak ultra-violet emmanations of certain coal constituents (2) may be capable of producing morbid changes in the lung over lengthy periods. The same author has investigated the methanol extracts of the vitrain constituents of several low rank coals (3) and has found them to posses definite antibiotic properties. Evans suggested that this may explain the inhibition of tuberculosis development often apparent in infected coal miners pneumocooniosis together with many of the apparent anomalies encountered in investigating the incidence of the disease. Thus, in accordance with Evans' theory, the incidence of lung disease in coal mines depends, not upon the silicosis hazard, but upon the relative quantities of coal macerals which are contained in the dust.

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